Comparison of diversion well substrates for the treatment of acid mine drainage, Bellvue Mine, West Coast, New Zealand

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by

Emma Jane Forbes

Department of Geological Sciences
University of Canterbury, Christchurch, New Zealand
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Abstract

Bellvue Mine is an abandoned mine north of Greymouth, Rapahoe, West Coast. Although abandoned since the 1970's, acid mine drainage is still being discharged from the mine and contaminating the nearby, Cannel Creek. A significant environmental problem globally, acid mine drainage is characterised by high dissolved metal concentrations and low pH conditions. As a result, Cannel Creek has become subject to ecosystem degradation and a loss of aquatic biodiversity.

Diversion wells are a method of passive treatment of acid mine drainage. A typical well consists of a cylinder-shaped container, filled with limestone aggregate, and a pipe centred down the well to allow water from an upstream dam to provide hydraulic head and entry to the system. Dissolution of the calcium carbonate raises the pH level, adds alkalinity and thus allows for precipitation of metal contaminants out of solution. Mussel shells are an alternative source of calcium carbonate and method of passive treatment. This research aimed to test the efficiency of a diversion well using mussel shells in treating acid mine drainage at Bellvue, in comparison to the more traditional diversion well using limestone.

An initial experiment was set up to test several combinations of variables which influence diversion well mechanics and function, to achieve optimal fluidization of substrate grains. These results could then be applied to diversion well installation at the site. The variables looked at were flow rates of water flowing into the well, the inlet pipe diameter, well height and diameter and substrate type and grain size. Several findings were made:

- Optimal fluidization occurred with inlet pipe sizes 32-50 mm.
- Grains were flushed over the well indicating the greater the well height, the greater the amount of substrate the well can contain, the more space for fluidization.
- The larger the well diameter, the less fluidization occurred horizontally.
- Optimal fluidization occurred with 2.36-10 mm limestone and 4.5-12 mm mussel shells.

Following this, a diversion well was installed at Bellvue. Limestone and mussel shells were tested individually in the well, a mixed substrate was also trialled. Chemical analysis and water quality data was collected to determine which substrate was more effective at treating acid mine drainage. Several findings were made:

- Initial operation of a diversion well allowed for effective improvements in water chemistry and quality, with each substrate. The pH levels were raised to near neutral and metals precipitated out of solution.
- The limestone proves to be the most effective treatment in this diversion well system compared to the mussel shells. Greater increases in pH levels and greater decreases in dissolved metal concentrations were achieved using the limestone substrate.
- Long term operation of a diversion well could not be achieved with this setup. The size of the well was too small for the volume of substrate necessary to achieve long term effective treatment.

Future work, involving larger scale treatment using a diversion well at Bellvue, will need to involve increasing the height and therefore, volume of the well, allowing the use of more substrate and thus, longevity of treatment. Limestone is the more desirable substrate for the most effective treatment in a diversion well system.

1

Introduction

1.1 Background

Acid mine drainage is a significant environmental problem globally. Sulphide-bearing minerals, exposed as a result of metalliferous and coal mining, interact with oxygen and water to produce acidic run-off, a considerable pollutant of many surface water systems. A long history of coal mining on New Zealand's West Coast has resulted in the production of acid mine drainage, increasingly having a negative effect on the quality of fresh water streams.

Bellvue, an abandoned coal mine north of Greymouth, is discharging acidic run-off into Cannel Creek. Past studies have shown sections of the creek, downstream of the mine site, have pH levels as low as 3.55 (Trumm & Cavanagh, 2006). Acidic discharge is also causing high dissolved metal concentrations (West, 2014). This has led to poor stream ecosystem health and low aquatic biodiveristy.

Passive treatment of acid mine drainage is a favourable method of treating contaminated waters at sites similar to Bellvue. These treatment systems are low maintenance, low cost and take advantage of the naturally occurring processes at the given site. A study carried out by West (2014) involved improving knowledge of site geochemistry and trialling small scale passive treatment systems at Bellvue. However, a diversion well, a form of passive treatment, has not been trailled at the site. There is a lack of understanding as to how effective the operation of a diversion well will be at treating acid mine drainage at Bellvue over time.

The presented research aimed to determine the efficiency of a diversion well at Bellvue Mine site for the treatment of acid mine drainage, and at the same time trial the mechanical operation of a diversion well using different substrates.

1.2 Acid Mine Drainage

1.2.1 Acid Mine Drainage Chemistry

Acid mine drainage is a significant environmental issue for mining industries globally. It is produced when sulphide-bearing minerals, such as pyrite (FeS_2), are exposed to oxygen and water, producing sulphuric acid and resulting in acidic effluent that contains elevated concentrations of metals and sulphates (Banks et al., 1997; Brown et al., 2002; Lottermoser, 2003; Akcil & Koldas, 2006). This process occurs naturally however, metalliferous and coal mining increases the exposure of sulphide minerals to oxygenated environments, accelerating the rate at which acidic drainage is produced (Banks et al., 1997; Brown et al., 2002; Lottermoser, 2003; Johnson & Hallberg, 2005; Akcil & Koldas, 2006). The acidity at a given site is controlled by the amount of acid producing minerals (typically sulphides) in comparison to the neutralizing minerals (for example, calcite and dolomite) present in the host rock being exposed (Rose & Cravotta, 1998; Skousen et al., 2017). The production of acid mine drainage is the shift from solid-phase acidity to solution-phase acidity. That is, the solid metals in the exposed rock are converted to dissolved metal contaminants, primarily iron and aluminium, when exposed to oxygen and water (Skousen et al., 2017). Acid mine drainage has negative effects on many surface water systems, causing a loss of environmental ecosystems and in some instances, implications for human health.

The following equations summarise the oxidation of sulphide minerals and the production of acid mine drainage (Banks et al., 1997; Brown et al., 2002; Lottermoser, 2003; Akcil & Koldas, 2006).

The oxidation of pyrite releases dissolved ferrous iron (Fe^{2+}), sulphate (SO_4^{2-}) and acidity (H^+):

$$FeS_2(s) + \frac{7}{2}\,O_2 + \,H_2O\, \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2H^+ \quad (1)$$

Ferrous iron (Fe^{2+}) produced can be oxidised to ferric iron (Fe^{3+}) at low pH conditions:

$$Fe^{2+} + \frac{1}{4}\,O_2 + \,H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \quad (2)$$

In conditions where the pH value is greater than 2.3 to 3.5, ferric iron is not soluble in water. It is precipitated as ferric hydroxide and results in less Fe^{3+} left in solution and a decrease in pH:

$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_3\,(s) + 3\,H^+ \quad (3)$$

In conditions where the pH value is less than 2.3 to 3.5, ferric iron is soluble in water. Any remaining ferric iron from equation (2), that does not precipitate as ferric hydroxide (3), can be used to further oxidise pyrite as the dominant oxidising agent. The subsequent reaction is rapid and strongly acid-producing:

$$FeS_2(s) + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+ \quad (4)$$

The above equations (1) and (4) assume pyrite is the mineral being oxidised. Although the weathering of pyrite has been well studied, other sulphide minerals are also subject to weathering and are associated with acid-generation and contaminated mine waters. The ability for acid mine drainage to be produced is largely dependent on local geology, including the nature of the sulphide ore, gangue minerals, acid producing and consuming minerals, grain sizes and surface areas, porosity and permeability of the deposit and the presence of micro-organisms (Brown et al., 2002). Thus, the production of acid mine drainage is largely site specific.

Acid mine drainage environments are often host to a variety of micro-organisms that favour acidic or neutral pH conditions and influence the rate at which acidity in contaminated waters is produced. For example, *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, are acidophilic bacteria which obtain energy by oxidising ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) (equation 2) (Rose & Cravotta, 1998; Schrenk et al., 1998; Nordstrom, 2000; Brown et al., 2002; Lottermoser, 2003). Thriving in pH 2 to 3 environments, these bacteria aid as a catalyst for the oxidation of Fe^{2+}, subsequently increasing the rate of acid generation (Lottermoser, 2003).

1.2.2 Environmental Impact

Acid mine drainage has significant environmental impacts, specifically to surface and ground water systems and can remain a problem long after mining activity has ceased. Discharge into water systems causes low pH conditions, increased trace element concentrations and ferric iron precipitates, degrading stream ecosystems and water quality.

Low pH conditions are a leading problem in terms of acid mine drainage impact. Acidic waters can destroy the natural bicarbonate buffer system. This system is a process that allows the natural

regulation of pH conditions of a water system. Acid mine drainage destroys this buffering ability below a pH of 4.2, where the reaction of free hydrogen with carbonate and bicarbonate ions allows the formation of carbonic acid. The carbonic acid then dissociates to form water and carbon dioxide (Brown et al., 2002).

$$H^+ + CO_3^{2-} \leftrightarrow HCO^{3-}$$
$$H^+ + HCO^{3-} \leftrightarrow H_2CO_3 \quad (5)$$

$$H_2CO_3 \rightarrow H_2O + CO_2 \quad (6)$$

Increased acidity due to the discharge of acid mine drainage causes changes in the optimal conditions required for aquatic organisms to sustain life (Brown et al., 2002). Acidic drainage from coal mines is a large contributor of acidity in water systems, where the presence of ferric iron allows for increased production of hydrogen ions and therefore, increased net acidity (Brown et al., 2002).

Acidic conditions allow higher solubility of trace metals and therefore, increases in dissolved metal availability (Brown et al., 2002). Excess metal concentrations are toxic to aquatic organisms. These also pose a threat to human drinking water quality, specifically if acidic mine drainage is being discharged into nearby water bodies used for human consumption.

Hydrolysis reactions of ferric iron allow the formation of ferric hydroxides, which form thick layers along stream beds. These ferric iron precipitates smother benthic organisms and can reduce sunlight penetrating the water column, reducing any potential photosynthesis reactions (Brown et al. 2002; Lottermoser, 2003).

1.2.3 Acid Mine Drainage and Coal Mining in New Zealand

Coal mining in New Zealand has been a significant industry sector, specifically for the West Coast region, since European settlement. The first coal mine in New Zealand dates to 1849 in Dunedin (Development West Coast et al., 2016). By the early 1900's the coal mining sector was New Zealand's primary energy source, with over a million tonnes of coal produced annually (Development West Coast et al., 2016). The demand for use in rail and shipping industries, specifically during World War II, meant coal became an essential resource for New Zealand's economy throughout most of the 20th century. By the 1960's and 1970's, with the switch to more

modern transport systems, the domestic demand for coal decreased (Development West Coast et al., 2016). However, over the past several decades, with fluctuations in oil prices and changes in the supply and demand of the steel industry, there was still a demand for coal, and the coal industry therefore, remained a significant sector in New Zealand's economy.

Several regions dominate the production of coal in New Zealand today. New Zealand's largest coal resource is in Southland and Central Otago and is lignite coal with a high moisture content, used mainly for local domestic industrial markets (MBIE, 2017). Coal production in Waikato is used for large domestic industry users, including the Huntley Power Station. The majority of New Zealand's coal exported overseas comes from the West Coast region, mainly due to being high quality bituminous and sub-bituminous coals (low ash and sulphur content), used in the production of steel (Trumm, 2007; MBIE, 2017). In 2015, 3.4 million tonnes of coal were produced in New Zealand, 1.4 million tonnes of which were exported overseas (MBIE, 2017).

In terms of consumption of coal in New Zealand, electricity generation is the largest domestic consumer. Industries including cement, lime, plaster, meat, dairy and other food processing, wool, timber and paper production plants are also large consumers of coal. Agricultural, transport and residential sectors account for small amounts of coal consumption (MBIE, 2017).

It is not until the past several decades that the environmental effects of the coal mining industry, specifically the production of acid mine drainage, have been properly recognised. With the West Coast region being a major producer of coal, most of New Zealand's acid mine drainage issues occur in this region (Trumm, 2007). The Resource Management Act of 1991 is legislation put in place to sustainably manage natural and physical resources and to minimise any adverse effects of activity on the environment. This includes the effect mining has on the environment, specifically the effect on surface and ground water systems (Simcock and Ross, 2014). Today, mining companies are responsible for the remediation and control of any effects mining has on the environment. With situations like Bellvue Mine, where abandoned mines are continuing to contaminate surrounding environmental systems, long after mining activities have ceased, local authorities (regional councils) are responsible for the management of the site and long-term restoration (Simcock and Ross, 2014).

1.3 Study Area

1.3.1 Bellvue Mine Location

Bellvue Mine operated over several decades beginning in 1927 until production ceased in 1970. The mine was opened as an extension to the larger James Mine, further northwest of Bellvue, along the same Brunner Coal seam. Bellvue Mine is approximately 12 km north of Greymouth, West Coast, situated on Cannel Creek (Figure 1.1). Several abandoned mines, including Bellvue, discharge water into Cannel Creek, which flows into the Tasman Sea, north of Rapahoe.

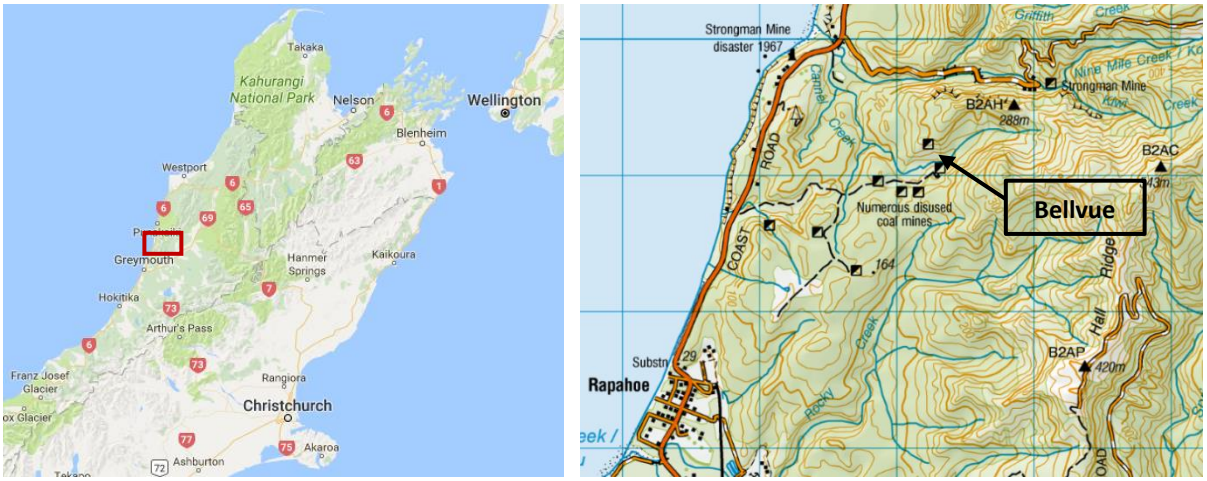

Figure 1.1. *Red square indicating location of Bellvue Mine site, West Coast, New Zealand (adapted from Google Maps (2017) and Land Information New Zealand (2016)).*

Bellvue Mine adit is located at the top of a 50 m long cascade. Contaminated water pools at the mine adit as the mine entrance has collapsed over time, damming water behind it. Acid mine drainage flows down the cascade, over a flat, non-vegetated area and into Cannel Creek (Figure 1.2).

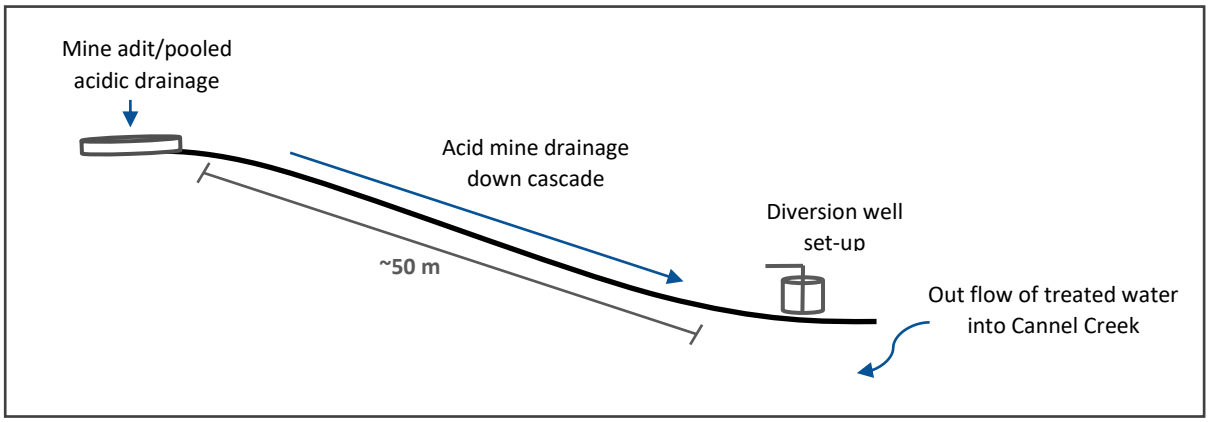

Figure 1.2. *Schematic of Bellvue Mine site showing path of acid mine drainage flow into Cannel Creek (not to scale).*

1.3.2 Local Geology

Geology of the Greymouth region includes Pre-Cretaceous sedimentary deposition of the Greenland Group, overlain by Late Cretaceous to Early Quaternary sediments that make up the Paparoa and Brunner Coal Measures, the Island Sandstone and Kaiata Mudstone Formations. Bellvue Mine lies within the Brunner Coal Measure (Gage, 1952; Nathan, 1978).

One of the most widespread basement rock units of the West Coast is the Greenland Group, which typically consists of thick, interbedded sequences of quartz-greywacke and argillite. It covers large areas in the northern sections of the Greymouth region, including Rapahoe. The Greenland Group is Late Cambrian to Ordovician in age (495± 18 m.y) and is typically 0.3-1.2 m thick, however some beds are up to 8.2 m (Nathan, 1978).

The Paparoa Coal Measures overlie the Greenland Group. This sequence consists of seven different lacustrine and fluvial mudstone and sandstone units, interbedded with coal seams. Towards the north-west regions of the West Coast, these grade into the youngest member of the sequence, the Dunollie Member, which is composed of coarser conglomerates, mainly of rounded greywacke, quartz and granite. The Dunollie Member, outcrops in the Rapahoe region, including sections upstream of Cannel Creek and Bellvue Mine site. The Paparoa Coal Measures are Late Cretaceous to Early Palaeocene in age (84 to 55.5 m.y) (Nathan, 1978).

The Brunner Coal Measures unconformably overlie the Paparoa Coal Measures. This sequence is predominately composed of quartz-rich sandstones, conglomerates, carbonaceous mudstones and interbedded coal seams and has been dated Eocene in age (43 to 37 m.y) (Nathan, 1978). These coal seams are typically low ash coals, high in sulphur (Gage, 1952; Nathan, 1978; Monteith, 2015).

The Island Sandstone conformably overlies the Brunner Coal Measures. This sequence is composed of light grey-brown calcareous fine sandstone and is also dated Eocene in age (43 to 36 m.y). The Island Sandstone largely outcrops over areas north of Rapahoe (Nathan, 1978).

The Kaiata Mudstone Member conformably overlies the Island Sandstone and makes up the oldest sequence of the Kaiata Formation. This unit consists of carbonaceous and calcareous mudstone and outcrops widely in regions north of Rapahoe. The Kaiata Mudstone is dated Late Eocene to Oligocene in age (36 to 34.3 m.y) (Nathan, 1974; Nathan, 1978). The Point Elizabeth Member, also part of the Kaiata Formation, overlies the Kaiata Mudstone and consists of grey-brown calcareous

mudstone, the upper parts of which are rich in glauconite. The Point Elizabeth Member is also dated Late Eocene to Oligocene in age (Nathan, 1974; Nathan, 1978).

Figure 1.3 shows these geological formations in the northern Greymouth region, from Point Elizabeth to Nine Mile Bluff, including the geology surrounding the Bellvue Mine area.

Stratigraphy of North Greymouth Region

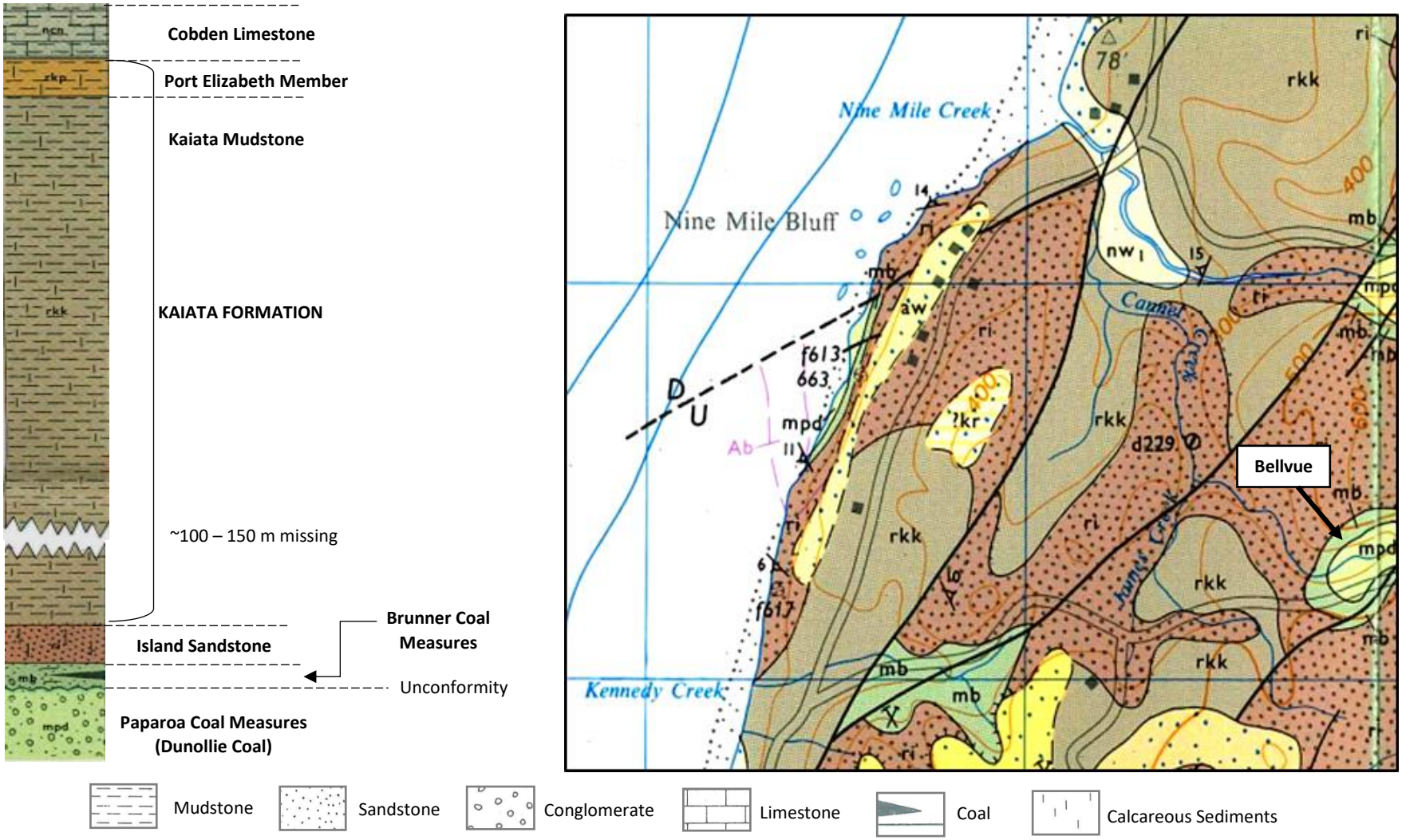

Figure 1.3. *Stratigraphy of north Greymouth region, including Bellvue Mine area. Note some geological formations are not included in the stratigraphic log, only the most relevant stratigraphy is shown (adapted from Nathan, 1978).*

1.3.3 Cannel Creek Geochemistry

Over the past decade, geochemical investigations have been carried out at the Bellvue Mine site in order to understand how to best remediate against acidic discharge and restore the water quality of Cannel Creek.

An investigative study carried out by Trumm and Cavanagh (2006) identified the basic geochemistry of Cannel Creek and the environmental issues associated with acidic run-off. Field measurements identified a significant decrease in pH of Cannel Creek waters from 5.79, upstream of the mine site, to 3.55, downstream of the site. The acidic run-off from the mine site had a pH of 3.01, indicating the acidic mine drainage from Bellvue was likely causing the decrease in pH of Cannel Creek. Concentrations of contaminants, specifically iron and aluminium, also increased downstream of the mine site. Total iron increased from 0.68 to 1.66 g/m^3. Total aluminium increased from 0.2 to 1.5 g/m^3. Concentrations of iron and aluminium in the acid mine drainage were high, 74 g/m^3 iron and 40 g/m^3 aluminium (total), indicating the mine discharge was affecting downstream chemistry (Trumm and Cavanagh, 2006).

Further geochemical data was collected by West (2014). Water samples from several areas at the site and along Cannel Creek were analysed. Table 1.1 outlines this analysis from different locations at the site.

Table 1.1 *Chemical analysis of water samples taken at several different locations at Bellvue. Data collected by West (2014) and is given as an average over the course of a year (West, 2014).*

Sample site	pH Level	DO (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	Zn (mg/L)	Sulphate (mg/L)
Pooled water at mine entrance (AMD source)	2.5	1.68	80.3	38.0	0.73	0.308	753.0
AMD at bottom of cascade	2.51	9.97	81.0	43.0	0.837	0.347	824.0
Cannel Creek – Upstream of Bellvue Mine	5.47	10.3	0.242	0.135	0.0083	0.0022	4.5
Cannel Creek – Down stream of Bellvue Mine	3.16	15.1	6.98	6.68	0.169	0.052	126.0

Decreases in pH level and increases in dissolved metal concentration occur in waters downstream of the Bellvue Mine acidic discharge. This indicates the acid mine drainage is directly affecting water quality of Cannel Creek.

Further data collection carried out by Trumm et al. (2016) gives a more recent chemistry of Bellvue Mine drainage and Cannel Creek. Water was sampled from pooled mine waters at the Bellvue Mine entrance and in Cannel Creek, both upstream and downstream of Bellvue Mine. Table 1.2 outlines the results.

Table 1.2 *Chemical analysis of sampled waters at Bellvue Mine site and Cannel Creek. pH is given as a range, dissolved metal concentrations are given as averages (Trumm et al., 2016).*

Sample site	pH Level	Fe (mg/L)	Al (mg/L)
Pooled water at mine entrance (AMD source)	2.28—3.01	69.0	39.0
Cannel Creek – Upstream of Bellvue Mine	4.60—7.28	0.29	0.14
Cannel Creek – Downstream of Bellvue Mine	2.76—4.30	6.49	5.91

Similarly, with previous studies, decreases in pH and increases in dissolved metal concentrations can be seen in Cannel Creek, downstream of Bellvue. Again, this indicates that acid mine drainage from Bellvue Mine is influencing water quality of Cannel Creek.

1.3.4 Cannel Creek Flow Rates

Flow rates from Bellvue Mine pool and from Cannel Creek were also measured by Trumm et al. (2016). Flows from the mine pool averaged 0.93 L/s, with a range of 0.041 to 30.3 L/s. However, less than 1% of flows were found to be greater than 5 L/s. Ninety-two percent of the flow rates are less than 2 L/s. Flow rates of Cannel Creek averaged 50 L/s, with a base flow of 2.7 L/s and a maximum of 3,800 L/s (Trumm et al., 2016).

Peaks in flow rates of Bellvue acid mine drainage (pooled mine water) and Cannel Creek do not occur at the same time. Flow rates of Cannel Creek peak 24 hours following high precipitation events. Flow rates of Bellvue acid mine drainage peak 48 hours after precipitation events. Therefore, the discharge of acidic drainage into Cannel Creek is greatest at the end of a storm event (Trumm et

al., 2016). Systems that can treat acid mine drainage during high precipitation events are therefore necessary for the long-term restoration of Cannel Creek.

1.4 Passive Treatment of Acid Mine Drainage

Passive treatment of acid mine drainage involves methods which require little or no continuous dosing of chemical reagents, are of low cost and take full advantage of the natural occurring processes at the given site. Treatment of acidic waters is often site specific and requires using a combination of techniques to fully treat contaminated water (Lottermoser, 2003). Generally, passive treatment methods raise pH levels and lower dissolved metal and sulphate concentrations, by either oxidation or reduction of contaminated water (Lottermoser, 2003).

1.4.1 Acid Neutralization Using Limestone

Many passive treatment systems are designed around the consumption of limestone, specifically the dissolution of calcium carbonate ($CaCO_3$), the principal component of limestone. Limestone is inexpensive and usually treatment systems using this substrate are easy to construct and maintain. The following reactions outline the dissolution of calcium carbonate which increases alkalinity and pH levels, neutralising acid mine waters, where $H_2CO_3 = [CO_2\ (aq)] + [H_2CO_3^0]$ (Cravotta & Trahan, 1996; Stumm & Morgan 1996; Skousen et al., 2017).

$$CaCO_3(s) + 2H^+ \leftrightarrow Ca^{2+} + H_2CO_3 \quad (7)$$

$$CaCO_3(s) + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (8)$$

$$CaCO_3(s) + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + OH^- \quad (9)$$

1.4.2 Previous Passive Treatment at Bellvue

It is only in the past several years that there has been a focus on the treatment of acid mine drainage at Bellvue. Only a few passive treatment systems have been trialled. Nothing so far, has been long term.

Small scale passive treatment systems were trialled by West (2014) in an attempt to identify the most effective form of remediation at the site. Two mussel shell reactors, a sulphate-reducing bioreactor and an anoxic limestone drain were tested over a 4-month period. One of the mussel shell reactors treated anoxic acid mine drainage from the mine adit, the other treated oxidised acid mine drainage from the base of the mine cascade. West (2014) found that the mussel shell reactor treating oxidised acid drainage, was the most effective passive treatment of acid mine drainage, raising the pH of discharge to neutral levels (7-8), thus raising the alkalinity and decreasing dissolved metal contaminants by over 90%. However, each system did not have the same residence time and therefore, an accurate comparison between each system could not be achieved (West, 2014). Based off this previous research, large scale mussel shell reactors were then installed at the site in 2017. Sampling of treated outlet waters has yet to be completed.

1.4.3 Diversion Wells

1.4.3.1 Diversion Well Function

A limestone diversion well are a form of passive treatment of acid mine drainage. Basic design and system function of a diversion well is described by Arnold (1991) and Schmidt and Sharpe (2002). A typical well consists of a circular casing, often sunk into the ground at a shallow level alongside a stream. Water is forced into the well by having an elevation difference that creates hydraulic head. This often involves damming water upstream. The water is flushed into the centre of the well through a pipe, typically 20-30 cm in diameter, and exists the pipe near the bottom of the well. The water then flows upwards, fluidizing the limestone substrate. Calcium carbonate reacts with the contaminated water to raise the pH and increase alkalinity, thus allowing for the removal of metal contaminants. Treated water is then piped from the well back into the stream (Arnold, 1991; Schmidt & Sharpe, 2002). A diversion well is usually 2/3 full of limestone, which needs to consist of greater than 85% of calcium carbonate for optimal results (Schmidt & Sharpe, 2002). This form of passive treatment is effective in that it treats acid mine drainage quickly, without long residence time, it does not require large amounts of space to install and is of low cost. However, regular maintenance is required in order to replace limestone and to clear any vegetation debris that can block the well intake (Arnold, 1991; Schmidt & Sharpe, 2002). Figure 1.4 illustrates diversion well function.

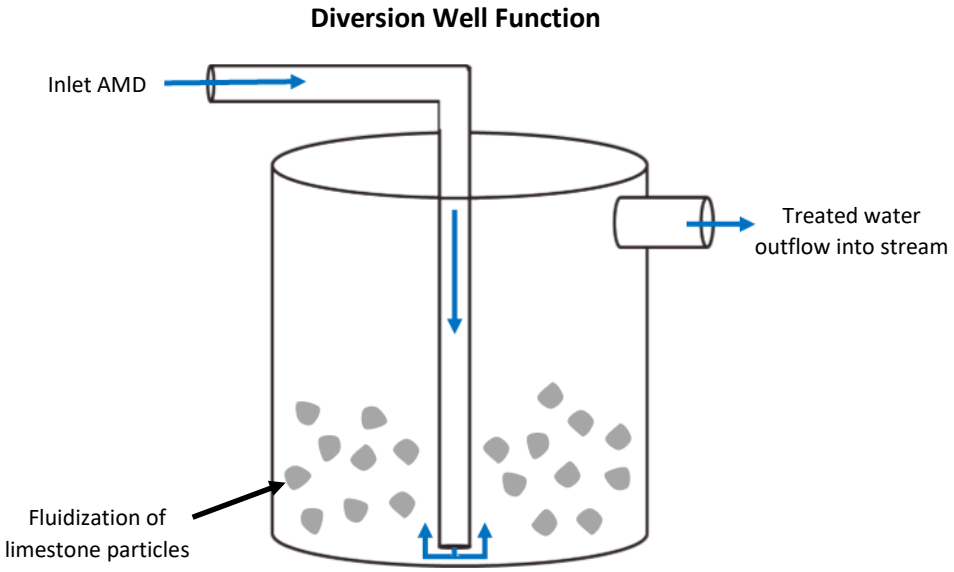

Figure 1.4 *Schematic diagram of a diversion well design and function. Contaminated waters from an upstream dam flushed down central pipe into limestone substrate, allowing for neutralization of acidic water. Treated water is then flushed through an outlet pipe back into stream.*

1.4.3.2 Previous Use of Diversion Wells

Arnold (1991) tested three diversion wells constructed at abandoned coal mine sites in Pennsylvania, United States. All wells were constructed as a 1.8 m deep, 1.8 m diameter concrete cylinder sunk into the ground. 20 cm diameter polyvinylchloride piping was used to feed water into the wells. Arnold (1991) recommends approximately 2.4 meters of hydraulic head is necessary to allow enough flow into the wells. Different sized limestone was trialled, ranging from flakes of 1.2 cm in diameter to aggregate 2.5 cm in diameter. The smaller sized limestone was easily washed out of the well and resulted in low calcium carbonate dissolution. Larger aggregate however, required more water flow to fluidize the system and provided less surface area for reactions to occur. Limestone 1-2 cm in diameter proved most successful (Arnold, 1991). In terms of consumption rates of limestone, Arnold (1991) suggests hard dolomitic limestone will react more slowly and is more resistant to crushing than a softer variety and will therefore last longer in the system. The diversion well systems used less than 0.7 m^3 of limestone per week (Arnold, 1991). Trial and error is recommended when determining consumption rates for the limestone substrate. Site specific chemistry results in the lack of ability to accurately calculate rates that can be used for all systems. Well operation over time showed that for water flows up to 0.14 m^3/s, the pH could be raised 1 to 2 units (Arnold, 1991).

Although diversion well system function and design has been well described, a lack of understanding remains on how the parameters of a system, such as well volume and substrate size, will need to be altered given different flow rates and different chemistries. In the past, trial and error has been used to determine what parameters work best for a given flow rate and a given mine site. A known form of passive treatment globally, diversion wells however, have not been previously been trailed in New Zealand. In addition to this, mussel shells have not previously been used in a diversion well as a substitute to the traditional use of limestone.

1.5 Research Aims and Objectives

This research trialled the efficiency of a diversion well at Bellvue Mine for the treatment of acid mine drainage, at the same time comparing the operation of a diversion well using limestone to that of mussel shells. This research aimed to improve current knowledge of the use of diversion wells for sites like Bellvue and to test the use of mussel shells as alternative diversion well substrate, whilst treating contaminated waters and improving stream water quality of Cannel Creek.

The thesis objectives included:

- Experiment with the mechanics of a diversion well to determine parameter relationships necessary for effective operation at the mine site.
- Install a diversion well system at Bellvue, trialling the use of limestone and mussel shells as substrates.
- Carry out chemical sampling and water quality parameters measurements of treated waters to test the efficiency of each substrate in a diversion well system.
- Compare the efficiency of mussel shells to that of limestone and use the results to determine if mussel shells are a more effective treatment of acid mine drainage.

1.6 Thesis Format

This thesis is formatted into five chapters. This chapter introduces the project, defines acid mine drainage in the context of the environmental effects of coal mining on the West Coast, describes the Bellvue Mine study area and gives an overview of previous use of passive treatment systems, with a description of a diversion well system and function.

Chapter two details the experimental setup carried out pre-field work, to determine the fluidization behaviours of different substrates within a diversion well system. This information was then used to determine what parameters (substrate grain size, well size, flow rates) were needed at Bellvue in order to achieve optimal fluidization of substrates with a setup in the field.

Chapter three focuses on the setup of a diversion well at Bellvue and the comparison of limestone to mussel shells as a diversion well substrate. Results are displayed in tables and graphs comparing chemical analyses (total and dissolved metal concentrations) and water quality parameters (pH levels, dissolved oxygen and electrical conductivity). Main findings and results are discussed.

Chapter four outlines the technical issues and limitations with the project; what could not be achieved and why.

Chapter five summarises the project. Objectives of this research are reiterated, and main findings outlined.

2

Diversion Well Mechanics

2.1 Introduction

Diversion wells operate based on the fluidization of substrate. This allows grains to bump into one another to prevent "armouring," the coating of substrate by iron precipitated out of solution. For a diversion well to be successful at treating acid mine drainage, the substrate must be able to fluidize. This often requires specific combinations of system parameters to achieve optimal mechanical operation.

To understand the mechanical operation of a diversion well system, experiments were carried out at the CRL Energy Ltd workshop. Several different parameters were varied to determine which combination of parameters work best to achieve fluidization of given substrates. The results were then used to determine the parameter combinations necessary for successful operation of a diversion well at Bellvue.

2.2 Method

A system was set up where water was pumped from a reservoir tank into a 110 L header tank positioned 1.5 m above ground. A PVC outlet from the header tank allowed vertical flow down into a container (wells) on the ground beneath. An 80 mm ball valve on the outlet pipe allowed control of water flow.

Several parameters were varied: 1) the size of the inlet pipe into the well, where 15 mm, 20 mm, 25 mm, 32 mm, 40 mm, 50 mm and 80 mm diameter pipe sizes were trialled (Figure 2.1); 2) flow rates were adjusted, using a range of inlet pipe sizes allowed for a range of flow rates, 0.5 L/sec to 1.6 L/sec average were trialled; 3) the substrate grain size, where aglime (powdered limestone), 2.36 – 5 mm limestone, 5 – 10 mm limestone (Figure 2.2), 4.5 – 12 mm mussel shells and whole/broken mussel shells were used (Figure 2.3) (any larger grain sizes would be too heavy to fluidize given other mechanical variables); 4) well dimensions (height and diameter). Four different size wells were used;

490 mm x 310 mm (Well One), 530 mm x 200 mm (Well Two), 250 mm x 190 mm (Well Three) and 270 mm x 260 mm (Well Four) (Figure 2.4). The limestone substrate was acquired pre-crushed and sieved to given sizes. The mussel shell substrate was acquired whole and some were crushed using a garden mulcher and sieved to size.

Figure 2.1 *Image of PVC piping used in fluidization experiments. From left to right; 80 mm, 50 mm, 40 mm, 32 mm, 25 mm, 20 mm and 15 mm inlet pipe. Top; 80 mm ball valve used to control flow of water from header tank into well.*

Figure 2.2 *The range of limestone grain sizes used in fluidization experiments. From left; aglime (powdered limestone), 2.36-5 mm limestone, 5-10 mm limestone.*

Figure 2.3 *The mussel shell grain sizes used in fluidization experiments. From left; whole/broken mussel shells and crushed 4.5-12 mm mussel shells.*

Figure 2.4 *Containers used as wells in fluidization experiment. Well One: 490 mm x 310 mm, Well Two: 530 mm x 200 mm, Well Three: 250 mm x 190 mm, Well Four: 270 mm x 260 mm.*

The pump was turned on to allow water flow through the system. No acidic water was used, the experiment designed to simply test fluidization mechanics rather than any chemical analysis. Each different well was trailled with each different grain size and each different inlet pipe, separately. Approximately one third of each well was filled with substrate (based on previous studies using diversion wells). A range of flow rates were achieved. Flow rates were measured using a bucket and stop watch method, where the well outlet water was captured in a container and the time taken for the container to fill up measured. The height and the diameter of fluidized grains was measured to determine the ability for fluidization and the behaviour of the substrate (Figure 2.5).

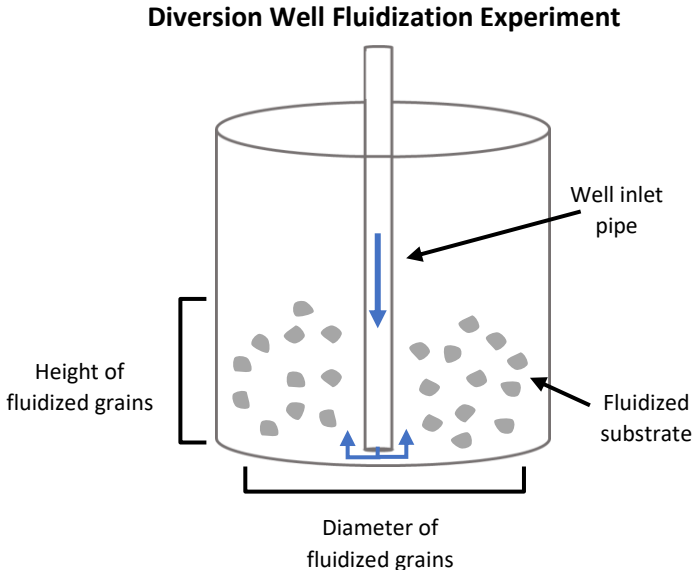

Figure 2.5 *Schematic of substrate fluidization, indicating the parameters (height and diameter of fluidized grains) measured during fluidization experiments.*

2.3 Results

2.3.1 Flow Rates Achieved

With this system setup, flow rates between 0.5 and 1.6 L/second could be achieved. The mean flow rates for each inlet pipe size are shown in Figure 2.6. Flow rates increased as inlet pipe size diameter increased however, less increase was seen with inlet pipe sizes greater than 32 mm.

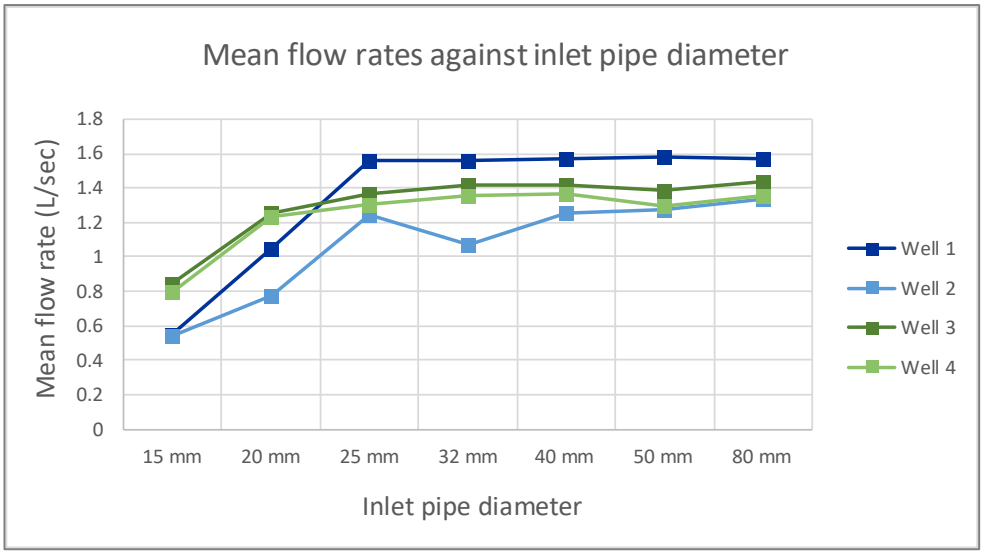

Figure 2.6 *Graph showing mean flow rates for each inlet pipe size diameter for each well size. The flow rate increases as the inlet pipe diameter increases however, less increase is seen with pipe sizes greater than 32 mm. The header tank capacity and the height the header tank sat from the ground was not large enough to achieve higher flow rates with the larger inlet pipe sizes. Pipe sizes less than 32 mm restrict maximum flow rates.*

2.3.2 Height of Substrate Fluidization

The height at which the substrate grains were fluidized to in each well is shown in graphs below (Figure 2.7). Optimal fluidization height was achieved with inlet pipe diameters 32 mm, 40 mm and 50 mm, where the substrates were reaching the maximum height of the well and being flushed out of the system. Minimal fluidization height was achieved with inlet pipe diameters less than 32 mm and greater than 50 mm. This is likely linked to what is known as the 'Bernoulli Effect,' the idea that there is a reduction in internal pressure when the velocity of water is increased, which occurs when the inlet pipe size is decreased. When the pressure is lost there is a lack of ability for grains to be fluidized vertically. When the inlet pipe diameter is increased, the velocity decreases, and similarly, a lack of fluidization.

Under the achieved flow rate conditions, the aglime proved to be too fine grained and most of the time, was flushed out of the wells. The whole/broken mussel shells also proved ineffective and showed little fluidization ability. The 2.36 – 5 mm limestone, 5 – 10 mm limestone and the 4.5 – 12 mm mussel shells showed the most ability to fluidize, specifically with inlet pipe sizes greater than 32 mm. However, the 5 – 10 mm limestone showed no ability to fluidize in Well One. This is likely because Well One had the largest dimensions and under the given flow rates, this size limestone was too large for grains to fluidize.

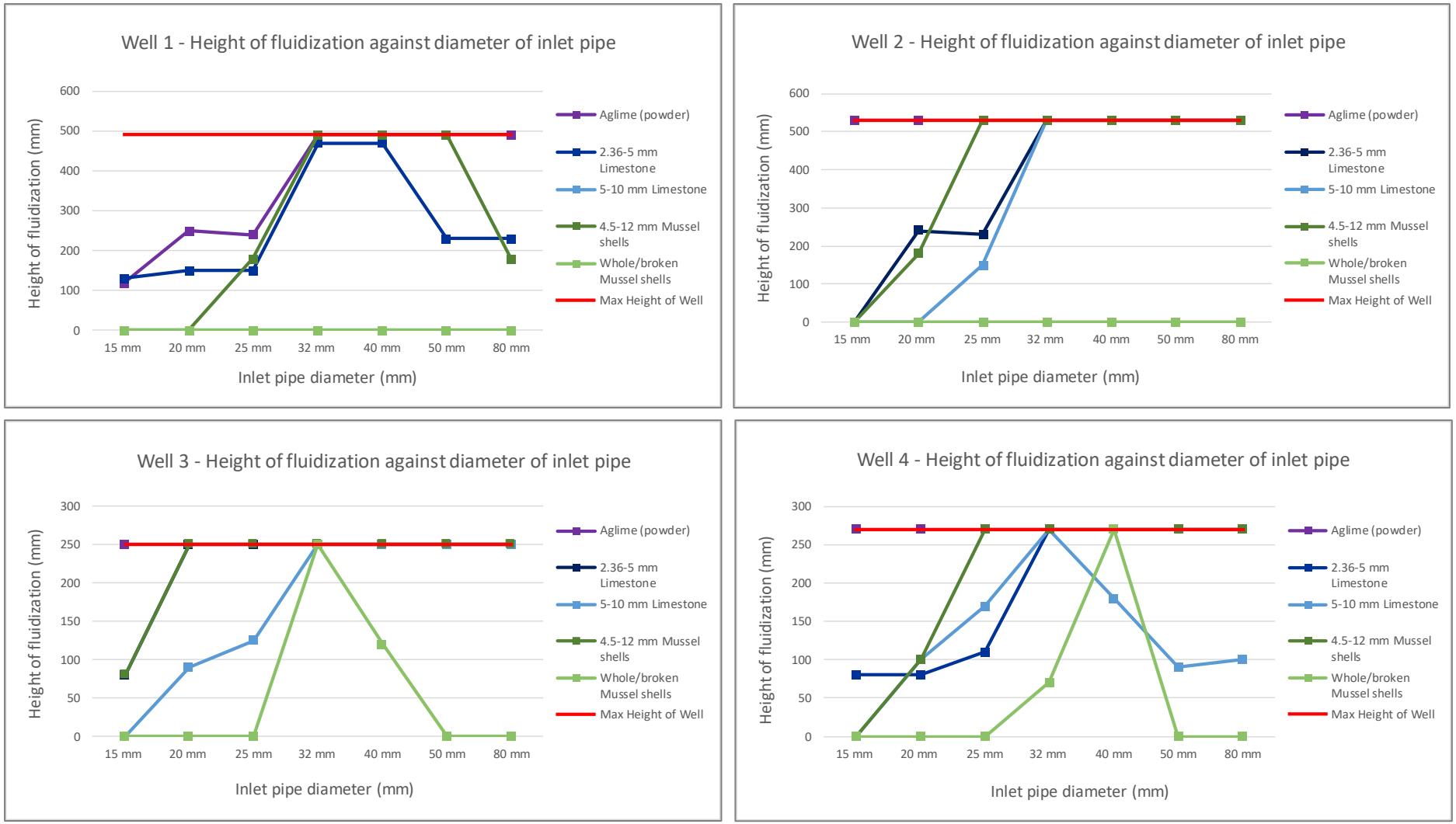

Figure 2.7 *Graphs showing the height of fluidization of diversion well substrate against the well inlet pipe diameter. The 32 mm, 40 mm and 50 mm inlet pipes allowed optimal fluidization height. Aglime and whole mussel shells proved ineffective. 2.36-5 mm limestone, 5-10 mm limestone and 4.5-12 mm mussel shells showed best ability to achieve optimal fluidization heights.*

2.3.3 Diameter of Substrate Fluidization

The diameter at which the substrate grains were fluidized to in each well is shown in graphs below (Figure 2.8). Similar trends to that of the height of fluidization can be seen. Optimal fluidization diameter was achieved with inlet pipe sizes 32 mm and 40 mm, where the substrates were fluidizing the whole diameter of the well. Minimal fluidization diameter was achieved with inlet pipe sizes less than 32 mm and greater than 50 mm. Again, this is likely linked to the 'Bernoulli Effect.' A loss of pressure when the inlet pipe size was decreased caused a lack of ability for grains to be fluidized horizontally. When the inlet pipe size was increased, a loss of velocity also caused a lack of fluidization.

The aglime, 2.36-5 mm limestone and the 4.5-12 mm mussel shells showed the most ability to fluidize horizontally. These grain sizes were being fluidized to the outer edges of the well, in some cases, the whole diameter of the well. The 5-10 mm limestone and whole/broken mussel shells showed the least ability to fluidize. Little horizontal fluidization was achieved with these sizes. This is likely because these sizes were too coarse for the flow rates attained. Substrates in Well One did not fluidize to the outer edges of the well, compared to the other wells used. This is likely because Well One had the largest diameter and the given flow rates were not high enough, and the system was not under enough pressure, to allow grains to fluidize the whole diameter of the well.

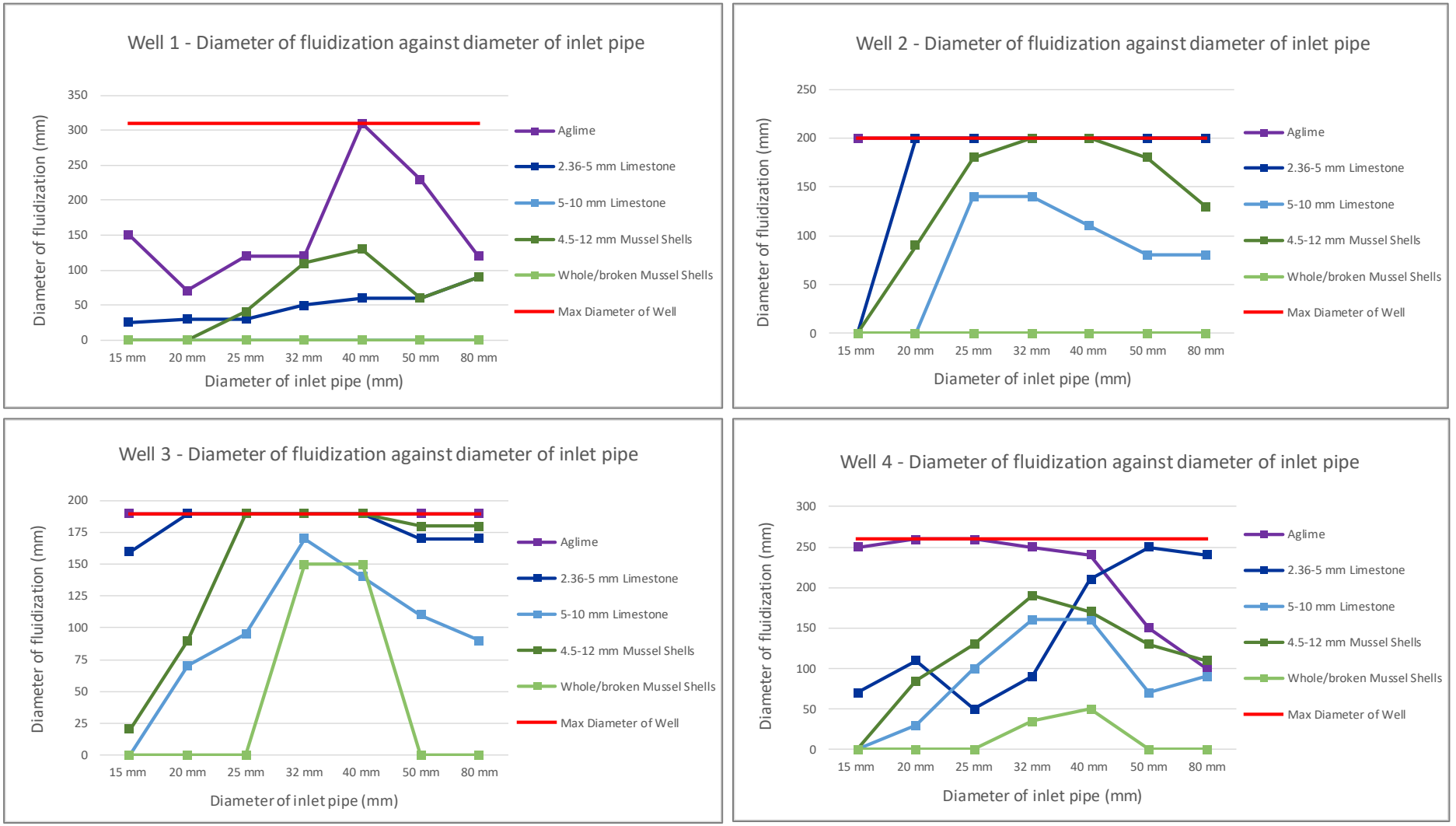

Figure 2.8 *Graphs showing the diameter of fluidization of diversion well substrate against the well inlet pipe diameter. The 32 mm and 40 mm inlet pipe sizes allowed optimal fluidization diameter. 5-10 mm limestone and whole mussel shells proved ineffective. The aglime, 2.36-5 mm limestone and 4.5-12 mm mussel shells showed best ability to achieve optimal horizontal fluidization.*

2.4 Summary

Achieving optimal fluidization involves having the substrate fluidize the full diameter of the well and a substantial percentage of the height of the well, without the substrate being flushed out. Variables which influence this are the mechanics of the well such as flow rates, inlet pipe diameter, well diameter and the substrate type and grain size.

In summary, several main findings could be made:

- The smaller inlet pipe diameters (< 32mm) reduced flow rates and therefore, reduced the ability for the substrate to fluidize.
- Larger inlet pipes (> 50 mm) increased flow rates however, the ability for the substrate to fluidize was not increased. This is likely linked to a decrease in velocity as the pipe size increases.
- The Aglime (powder) was too fine to be fluidized and was flushed out of the system.
- The whole/broken mussel shells showed minimal fluidization ability (< 1.5 L/sec flow rates).
- The 2.36 – 5 mm, 5 – 10 mm limestone and the 4.5 – 12 mm mussel shells showed the most ability to fluidize, specifically with inlet pipe sizes >32 mm.
- Optimal fluidization height occurred with inlet pipe sizes 32 – 50 mm.
- The greater the well height, the more substrate the well can contain, the more space for fluidization. Substrates < 12 mm were being flushed out of the well with pipe sizes 32 – 50 mm and flow rates of 1 to 1.6 L/sec, indicating a greater well height could be used and fluidization would still occur.
- The larger the diameter of the well, the less ability for the substrate to fluidize to the outer edge of the well (less fluidization diameter).

These fluidization experiments allowed an understanding of how the mechanics of a diversion well system are dependent on one another in order to achieve desired fluidization of substrate grains. These results were applied to the diversion well design at Bellvue, with some alterations depending on site specific conditions.

3

Diversion Well Passive Treatment

3.1 Overview

A diversion well system was installed at the Bellvue Mine site, designed to test the efficiency of a diversion well using limestone substrate compared to that of mussel shells, to determine which substrate was more effective at treating acid mine drainage.

The system consisted of a well (blue barrel), linked to two intermediate bulk containers (IBC's). Acidic water, siphoned from pooled mine waters, flowed vertically into the well and into the treatment media. Treated water then exited the well and flowed into IBC 1 and 2 consecutively. The treated water then flowed out IBC 2 and back into nearby Cannel Creek. Crushed limestone and mussel shells were tested as substrates separately over several site visits throughout the year. Treated water was sampled over the course of the system operation (several hours). Water quality parameters were also measured using field instruments.

Metal concentrations and water quality parameters were then analysed. Comparison of results were made between the limestone treatment and mussel shell treatment.

With this given diversion well setup, the limestone substrate proved to be more effective at producing alkalinity, raising the pH level and allowing for metal contaminants to precipitate out of solution, thus being a more effective passive treatment of acid mine drainage.

3.2 Method

The primary purpose of this research was to determine the efficiency of a diversion well using mussel shells for the treatment of acid mine drainage at Bellvue Mine, in comparison to that of the more traditional diversion well using limestone. To achieve this, a practical experimental setup was designed to test the use of mussel shells and limestone in a diversion well to determine which

substrate is more effective at raising the pH level of acidic waters thus, allowing for the removal of metal contaminants.

3.2.1 System Set Up

Experimental setup consisted of using a 110 L barrel (800 x 400 mm) as the diversion well, with two intermediate bulk containers (IBC) connected to the well in series. This size well was determined based on fluidization experiments, mentioned in previous chapters, and on the availability at the time. The use of the IBCs was to increase residence time of the water flowing through the system. Substrate grains would be transported into the IBCs from the well, allowing further contact between grains and acidic water, resulting in further dissolution of grains and thus treatment of acid mine drainage. Acidic water was siphoned from pooled mine waters, using three pre-existing 25 mm alkathene pipes, to a 50 mm PVC pipe which fed directly to the bottom of the well. This inlet pipe rested on the base of the well and was perforated with 10 mm holes, equalling the cross-sectional area of the pipe. This was to increase velocity of the water flowing into the well therefore, increasing the ability for fluidization of substrate grains towards the outer edges of the well. From the well, IBC 1 was connected down gradient using a 50 mm PVC pipe, similarly from IBC 1 to IBC 2. This setup allowed siphoned acidic water to flow down into the bottom of the well, up through the substrate, out of the well and through the connected IBCs, exiting the system through a 50 mm hole in IBC 2 which allowed water flow back into Cannel Creek. Acidic water, which would otherwise flow down the mine cascade into Cannel Creek, is simply diverted through the treatment system before being flush back downstream. The following images show this diversion well system.

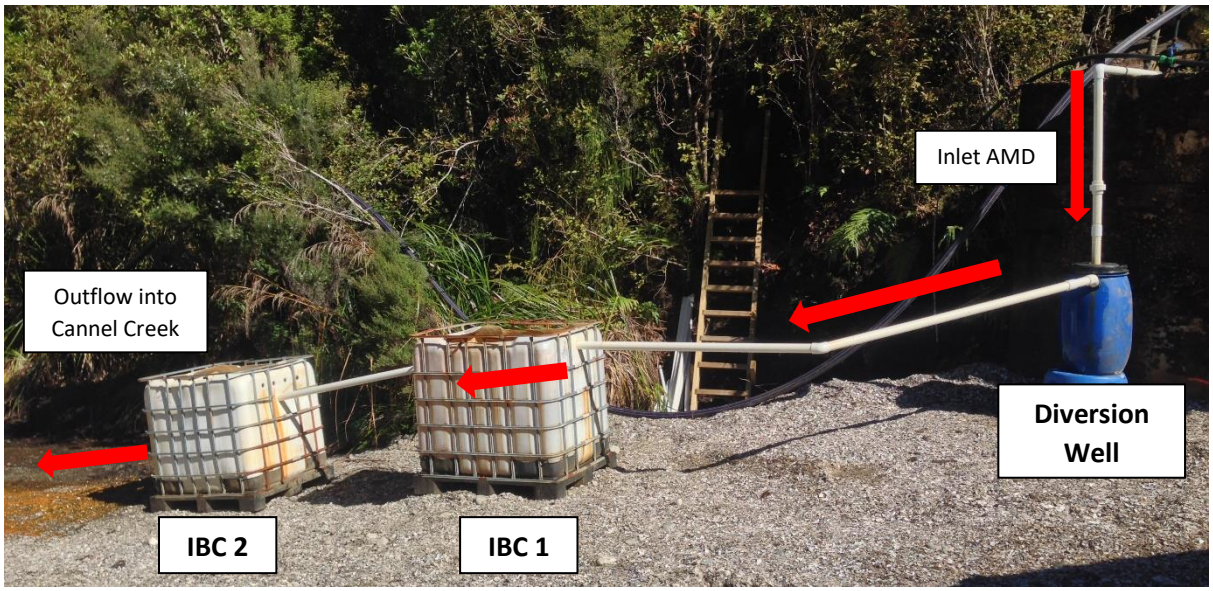

Figure 3.1 *Image of diversion well set up at Bellvue Mine site. Inlet AMD enters the well where fluidization of substrate occurs, treated water then flows through each IBC where further dissolution of substrate and neutralization reactions occur. Treated water then flows down into Cannel Creek.*

Figure 3.2 *The 110 L barrel used as diversion well. AMD enters the well through a 50 mm PVC inlet pipe seen vertically in photo. Substrates are fluidized, and treated water leaves the well and flows into IBC 1.*

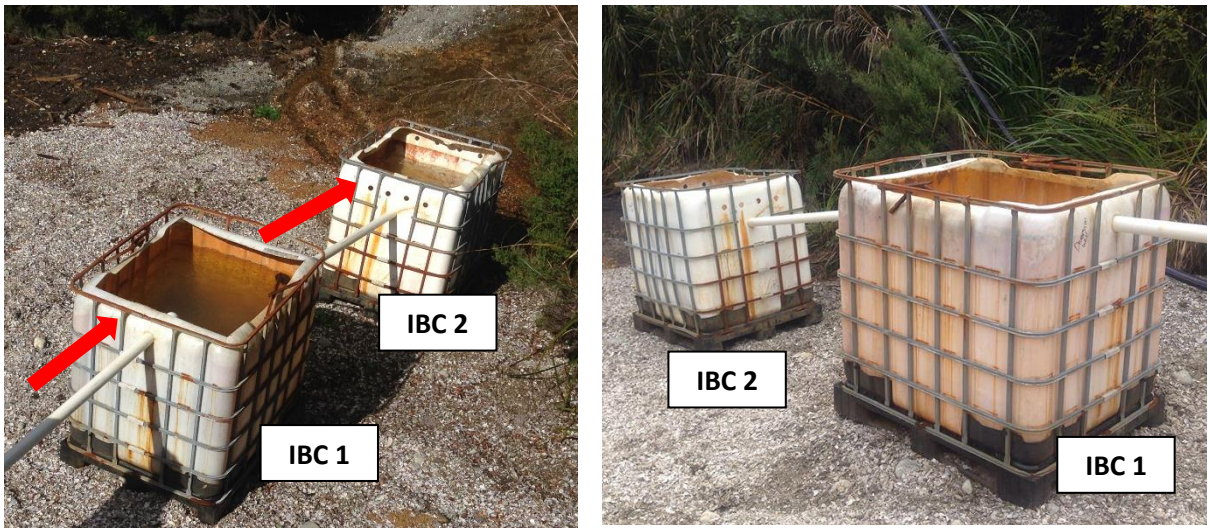

Figure 3.3 *Aerial and side view of IBC section of setup at Bellvue site. Arrows indicate direction of treated water flow through system.*

Figure 3.4 *A) IBC 1 full of water being treated with limestone substrate. AMD has entered the diversion well and fluidized the limestone substrate. The water has then flowed into the IBCs where further dissolution occurred, shown here in image A. B) IBC 2 outlet of treated water which flows down into Cannel Creek.*

3.2.2 Residence Times and Flow Rates

Residence time of the setup was increased by having the two IBC's linked to the diversion well in series. This increases the time the water flows through the system, subsequently increasing time for water and substrate grain contact, thus allowing optimal dissolution of calcium carbonate and associated neutralisation reactions.

The residence time of the system can be calculated as follows:

$$\frac{Amount\ of\ water\ in\ reservoir}{Outflow\ (or\ inflow) at\ a\ steady\ state} = Residence\ time$$

$$\frac{Well + IBC\ 1 + IBC\ 2}{Outflow\ rate} = Residence\ time$$

$$\frac{(110\ L + \ 800\ L + 650\ L)}{2.4\ L/sec} = 10\ Minutes\ 48\ seconds$$

This calculation assumes the diversion well is empty (no substrate has been added) and that the flow rate into and out of the system are the same and remain constant.

The residence time of the system was more accurately calculated in the field by simply timing how long it took the whole system to fill with water, with the diversion well containing substrate. The result was very similar, 10 minutes, 3 seconds.

The system took 10 minutes and 3 seconds to fill. The initial sampling took place as soon as water started flowing out of the IBC 2 outlet, back into Cannel Creek, that is 10 minutes, 3 seconds after the valves were turned on allowing water flow through the system. The 15-minute sampling then took place 15 minutes following the initial sample, and so on.

Flow rates were taken throughout the experiments using a bucket and stop watch method. Average flow rates of water flowing out of IBC 2 was 2.4 L/second, the same as for inflowing water.

3.2.3 Substrates

Limestone and mussel shell substrates were tested in the diversion well separately. A mixed substrate was also tested. Using trial and error, and based on fluidization experiments, substrates were crushed to allow the grains to fluidize in the well and reduce the effects of armouring. In terms of substrate size, 0-5 mm limestone and 0-4.5 mm mussel shells were used. The limestone was sourced at this size from Springfield Lime Company Ltd. The mussel shells were sourced whole, as a waste product, from United Fisheries, and were crushed using a garden mulcher and sieved to size. Previous passive treatment of acid mine drainage using diversion wells suggests having the well 1/2

to 2/3 full of substrate (Arnold, 1991). Sixty litres of substrate was in the well in each test, equating to just over half of the well volume. The given site conditions, specifically the flow rates, velocity and pressure of the water entering the well, meant that greater amounts of substrate would cause the system to block up and grains would not fluidize. Figure 3.5 shows the grain size of limestone and mussel shells used in the experiment.

Figure 3.5 *Image of 0-5 mm limestone (left) and 0-4.5 mm mussel shells (right) used in diversion well. Pencil for scale.*

3.2.4 Data Collection

Both limestone and mussel shells were tested multiple times over several different field trips to the mine site. Each test consisted of running the system and collecting data over several hours to observe changes in water quality and chemistry over time.

Treated water samples and water quality parameters were taken from the system outlet as soon as water filled the system and began flowing out IBC 2, (initial), after 15 minutes of outflow, 30 minutes, 1 hour and after 18 hours. An inlet sample was taken from the acidic water entering the well at the beginning of each test.

Each water sample was laboratory analysed for the following:

- Water for total metals – unfiltered, preserved with nitric acid

- Water for dissolved metals – filtered using a 0.45 micron filter, preserved with nitric acid
- Water for sulphate – unfiltered, not preserved

The samples were then sent to Hills Laboratories for chemical analysis. Previous analysis of acidic water at Bellvue indicated elevated levels of Al, Fe, Mn, Ni and Zn. These metals were therefore, chosen for analysis in this project.

The pH level, dissolved oxygen and electric conductivity allow an indication of general water quality of surface waters. These parameters were tested during data collection to give an idea of how the water quality was affected after treatment using limestone and mussel shells.

The pH level is a measure of the concentration of hydrogen ions in the water. Surface water systems with pH levels below 6 are deemed unacceptable as highly acidic waters cause persistent stresses on organisms often leading to a decline in aquatic ecosystems and loss of keystone species (Davis-Colley et al., 2013; NIWA, 2016). When pH levels increase, metal contaminants precipitate out of solution. It is therefore, a crucial parameter necessary to compare water quality pre-and post-diversion well treatment.

Dissolved oxygen is also a significant indicator of stream water quality. Decreasing dissolved oxygen levels inhibit the reproduction of aquatic organisms, leading to stream ecosystems similar to Cannel Creek, where the stream in virtually inhabitable. Photosynthesis is a major process controlling dissolved oxygen levels in surface water systems (Davis-Colley et al., 2013; NIWA, 2016). With little plant growth, even less oxygen is released into the stream. Testing dissolved oxygen levels is necessary to give an idea of water quality, especially in terms of the biological aspect of stream health.

Electric conductivity is a measure of the ability for ions in water to conduct electricity. These ions come from dissolved salts and inorganic materials. Electric conductivity is therefore, often an indicator of the nutrient content of a water body (NIWA, 2016).

Collection of these water quality parameters involved using a calibrated YSI to obtain measurements of water sampled at each time frame. The YSI probe was left in the water being sampled for a few minutes to increase accuracy of the readings.

The sampling equipment used for data collection, raw data showing chemical analysis and water quality parameters and the original Hills Laboratory reports, can be found in the attached appendices.

3.3 Results

This section discusses the following; inlet acid mine drainage chemistry, limestone treatment results, mussel shell treatment results, a comparison between each substrate and analysis of using a mixed substrate and a summary.

Table 3.1 below shows the results of treatment using a diversion well set up at Bellvue. Total and dissolved metal concentrations and water quality parameters, for treated water using limestone and mussel shells are compared to inlet acidic mine water, thus allowing comparison of which substrate proved more effective at AMD treatment. Results shown are given as averages. To average the pH values correctly, a formula was used to calculate the hydrogen ion concentration for each pH value (10). The mean hydrogen ion concentration was then calculated and converted back to a pH value (11). Formulas used are as shown:

$$[H^+] = 10^{-pH} \tag{10}$$

$$pH = -log[H^+] \tag{11}$$

Table 3.1 *Total and dissolved metal concentrations for inlet acid mine drainage, treatment using limestone and treatment using mussel shells and treatment using a mixed substrate. Note, LS - limestone, MS – mussel shells, Mix – mixed substrate, x – no data acquired. These results are averages taken from raw data sets found in appendix E.*

		Inlet AMD	Initial			15 minutes			30 minutes			1 hour			18+ hours		
			LS	MS	Mix	LS	MS	Mix	LS	MS	Mix	LS	MS	Mix	LS	MS	Mix
Metal Concentrations (g/m^3)	**Total Al**	36	20.6	30.3	24	35.5	36	29	33	35.3	30	34	36.3	31	28.5	37	x
	Dissolved Al	37	0.55	26.3	13.8	23.7	36.5	30	31.3	35	33	36	36.3	33	31	39.7	x
	Total Fe	54.2	30.8	60.3	55	56	83	54	40.3	66.3	56	33	68	56	37.5	70.3	x
	Dissolved Fe	54.2	15	41.1	39	53	75.5	46	33.3	64.3	54	29.5	67.7	55	32.5	73.7	x
	Total Mn	0.7	0.79	0.76	0.79	0.825	0.805	0.74	0.715	0.74	0.71	0.723	0.74	0.72	0.63	0.73	x
	Dissolved Mn	0.711	0.78	0.73	0.75	0.89	0.82	0..71	0.733	0.74	0.71	0.707	0.73	0.69	0.615	0.72	x
	Total Ni	0.12	0.125	0.121	0.118	0.137	0.131	0.116	0.12	0.126	0.114	0.119	0.122	0.117	0.106	0.124	x
	Dissolved Ni	0.121	0.118	0.121	0.11	0.14	0.136	0.113	0.121	0.124	0.112	0.119	0.126	0.11	0.105	0.127	x
	Total Zn	0.316	0.268	0.29	0.26	0.33	0.34	0.27	0.293	0.3	0.27	0.31	0.3	0.27	0.285	0.31	x
	Dissolved Zn	0.317	0.235	0.29	0.25	0.335	0.34	0.26	0.288	0.31	0.27	0.303	0.31	0.27	0.255	0.323	x

Table 3.2 *Water quality parameters for inlet acid mine drainage, treatment using limestone and treatment using mussel shells and a mixed substrate. Note, LS - limestone, MS – mussel shells, Mix – mixed substrate, x – no data acquired. These results are averages taken from raw data sets found in appendix E.*

		Inlet AMD	Initial			15 minutes			30 minutes			1 hour			18+ hours		
			LS	MS	Mix	LS	MS	Mix	LS	MS	Mix	LS	MS	Mix	LS	MS	Mix
Water Quality Parameters	pH Level	2.69	5.86	3.79	4.66	3.34	3.11	3.62	3.22	2.99	3.24	3.06	2.93	3.13	2.84	2.8	x
	Sulphate (g/m^3)	717.1	1,007.5	746.7	710	800	780	710	685	750	700	696.7	756.7	710	600	770	x
	DO (%)	42.26	52.83	46.7	54.4	55.1	48.7	47.8	45.87	39.35	45.7	41.9	35.45	49.8	58.2	54.75	x
	EC (µs/cm)	1,471.8	934	1,411.5	1,862	1,047	2,030	1,844	911	1,550	2,008	889	1,602.5	2,124	1,068	1,793	x

3.3.1 Inlet Acid Mine Drainage

Acidic mine water, pooled at the mine adit, was siphoned into the diversion well system during testing. This acidic inlet water was analysed during each test, chemical sampling was carried out and water quality parameters were measured. This gave a control that the limestone and mussel shell treatment results could be compared to.

Average dissolved metal concentrations are as follows; Al 37 g/m^3 (ranged from 27 to 54 g/m^3), Fe 54.17 g/m^3 (29 to 115 g/m^3), Mn 0.71 g/m^3 (0.52 to 0.96 g/m^3), Ni 0.122 g/m^3 (0.087 to 0.165 g/m^3), Zn 0.32 g/m^3 (0.21 to 0.45 g/m^3), whilst sulphate averaged 717.1 g/m^3 (530 to 990 g/m^3).

The average pH level was 2.69 (ranged from 2.5 to 2.95). Averaged dissolved oxygen was 42.26 % (30.8 to 67.8 %). Averaged electric conductivity was 1,471.8 µs/cm (1,100 to 2,471 µs/cm).

3.3.2 Limestone Results

3.3.2.1 Water Chemistry

One sample was taken for each total, dissolved and sulphate analysis for each time interval (inlet acid mine drainage, initial outlet, 15 minutes, 30 minutes, 1 hour and 18 hours). This was repeated four times using limestone substrate over several trips to the Bellvue site. Initial sampling of treated water using the limestone substrate showed immediate improvements in water chemistry and quality. Initially, dissolved metal concentrations decreased compared to the inlet untreated, acid mine drainage. Initial dissolved Al concentrations averaged 0.54 g/m^3 (ranged from 0.065 to 1.81 g/m^3), Fe averaged 14.97 g/m^3 (3.4 to 22 g/m^3), Mn averaged 0.7 g/m^3 (0.62 to 1.06 g/m^3), Ni averaged 0.118 g/m^3 (0.95 to 0.158 g/m^3) and Zn averaged 0.23 g/m^3 (0.163 to 0.4 g/m^3), whilst sulphate averaged 1000.7 g/m^3 (570 to 1970 g/m^3).

After initial treatment of water, improvements in chemistry started to decrease. Water being treated, after 15 minutes of diversion well operation, showed slight increases in dissolved metal concentrations from initial results. Dissolved Al averaged 23.65 g/m^3 (ranged from 15.3 to 32 g/m^{3+}). Fe averaged 53 g/m^3. No range is given for dissolved Fe concentrations for 15-minute sampling. This is due to outliers being removed from the final data set therefore, the remaining data value is still higher than expected (Figure 3.6). The expected dissolved Fe concentration would have been less than concentrations seen at 30 minutes, 1 hour and 18 hour intervals. Mn averaged 0.89 g/m^3 (0.76

to 1.02 g/m^3), Ni averaged 0.14 g/m^3 (0.159 to 0.2 g/m^3), Zn averaged 0.34 g/m^3 (0.27 to 0.4 g/m^3) and sulphate averaged 800 g/m^3 (700 to 900 g/m^3).

Thirty minutes of diversion well operation showed more increase in dissolved metal concentrations. Al averaged 31.25 g/m^3 (ranged from 25 to 39 g/m^3), Fe averaged 33.33 g/m^3 (22 to 55 g/m^3), Mn averaged 0.73 g/m^3 (0.58 to 0.97 g/m^3), Ni averaged 0.12 g/m^3 (0.10 to 0.16 g/m^3, Zn averaged 0.29 g/m^3 (0.22 to 0.41 g/m^3) and sulphate averaged 685 g/m^3 (580 850 g/m^3).

After 1 hour, dissolved Al averaged 36 g/m^3 (ranged from 29 to 50 g/m^3), Fe averaged 29.5 g/m^3 (27 to 32 g/m^3), Mn averaged 0.71 g/m^3 (0.56 to 0.94 g/m^3), Ni averaged 0.12 g/m^3 (0.10 to 0.16 g/m^3), Zn averaged 0.30 g/m^3 (0.24 to 0.42 g/m^3) and sulphate averaged 697 g/m^3 (580 to 920 g/m^3).

Water flowing through the diversion well system after 18 hours of operation showed little improvement in comparison to the inlet acid mine drainage chemistry. After this length of time all the very fine-grained limestone had left the system, the amount of remaining substrate and the grain size were not sufficient to neutralise acid waters. The remaining substrate also showed less fluidization ability. Only a small section around the central inlet pipe was being fluidised (approximately 400 mm in fluidization height and 150 mm diameter) and by this stage, armouring of the substrate in Fe precipitates had occurred, inhibiting dissolution of grains. Dissolved Al concentration averaged 31 g/m^3 (ranged from 30 to 32 g/m^3), Fe averaged 32.5 g/m^3 (28 to 37 g/m^3), Mn averaged 0.62 g/m^3 (0.61 to 0.62 g/m^3), Ni averaged 0.11 g/m^3 (0.10 to 0.11 g/m^3), Zn averaged 0.26 g/m^3 (0.25 to 0.26 g/m^3) and sulphate averaged 600 g/m^3 (590 to 610 g/m^3).

Dissolved metal concentrations for diversion well treatment using a limestone substrate are displayed in Figures 3.6 and 3.7 below.

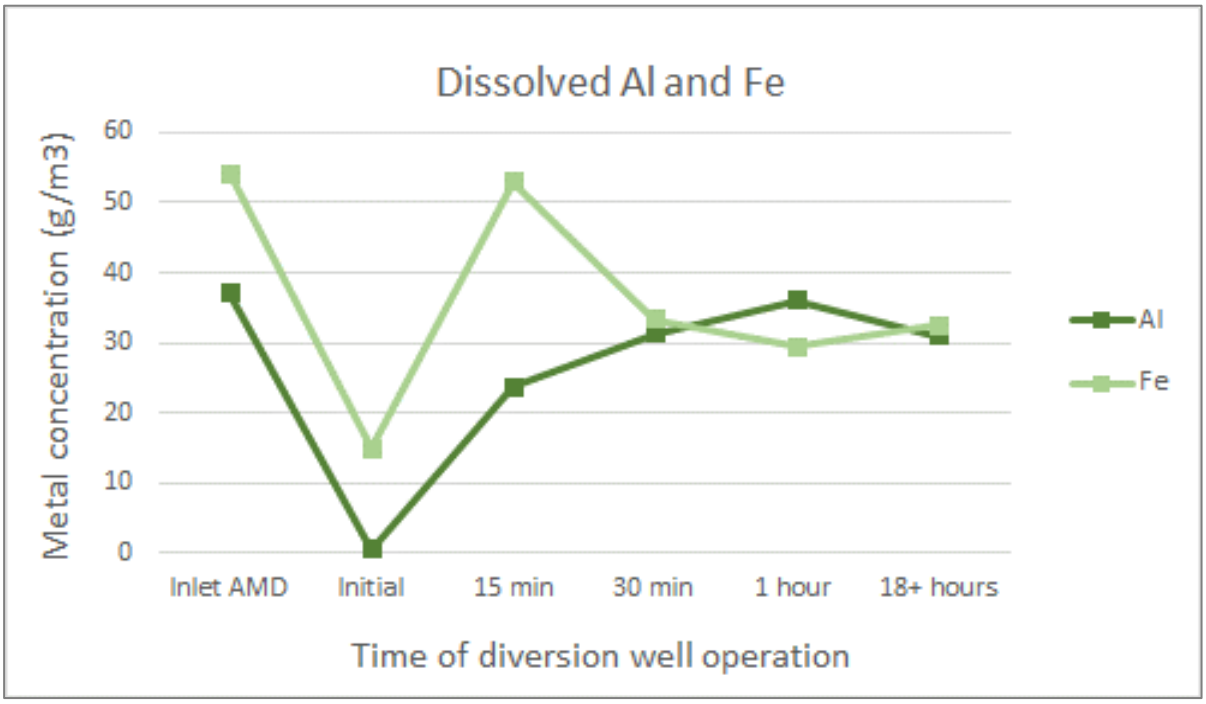

Figure 3.6 *Dissolved Al and Fe concentrations of treated waters using limestone substrate in a diversion well system.*

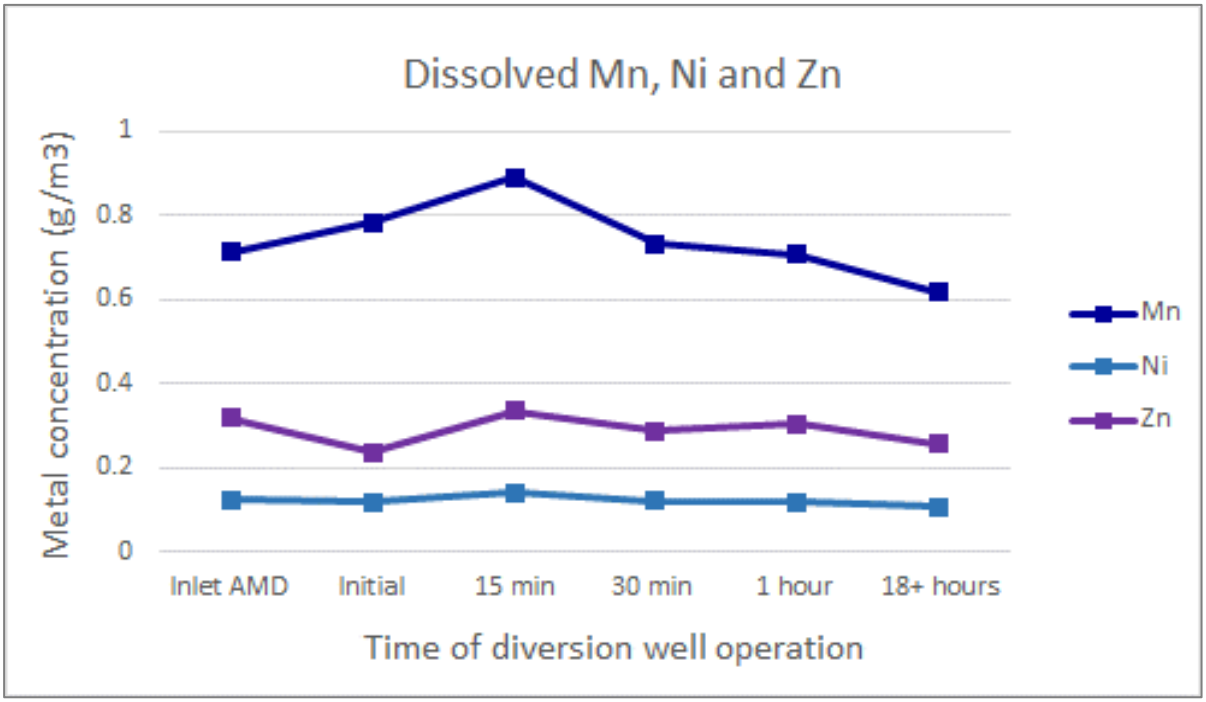

Figure 3.7 *Dissolved Mn, Ni and Zn concentrations of treated waters using limestone substrate in a diversion well system.*

3.3.2.2 Water Quality

Water quality data was collected using field instruments once for every time interval (inlet acid mine drainage, initial outlet, 15 minutes, 30 minutes, 1 hour and 18 hours). This was repeated four times using limestone substrate over several trips to the Bellvue site. Figure 3.8 shows average pH levels of treated water using limestone. Water quality parameters of treated waters showed immediate improvements. Initially, average pH levels increased to 5.86 (ranged from 5.6 to 6.2), dissolved oxygen increased to 52.8% and electric conductivity decreased to 932.7 µs/cm.

After 15 minutes, pH levels only reached an average 3.34 (3.04 to 5.3), dissolved oxygen 55.1% and electric conductivity 1047 µs/cm.

After 30 minutes, pH levels averaged 3.22 (2.89 to 3.83), dissolved oxygen 45.86% and electric conductivity 911.3 µs/cm.

After 1 hour, pH levels averaged 3.06 (3.05 to 2.9), dissolved oxygen 41.9% and electric conductivity 888.5 µs/cm.

After 18 hours of diversion well operation, average pH levels had decreased again to 2.84 (2.74 to 2.98), similar to the inlet acid mine drainage pH levels. Dissolved oxygen averaged 58% and electric conductivity increased again to an average 1067.5 µs/cm. This indicates that improvements in the quality of treated water decreased over time.

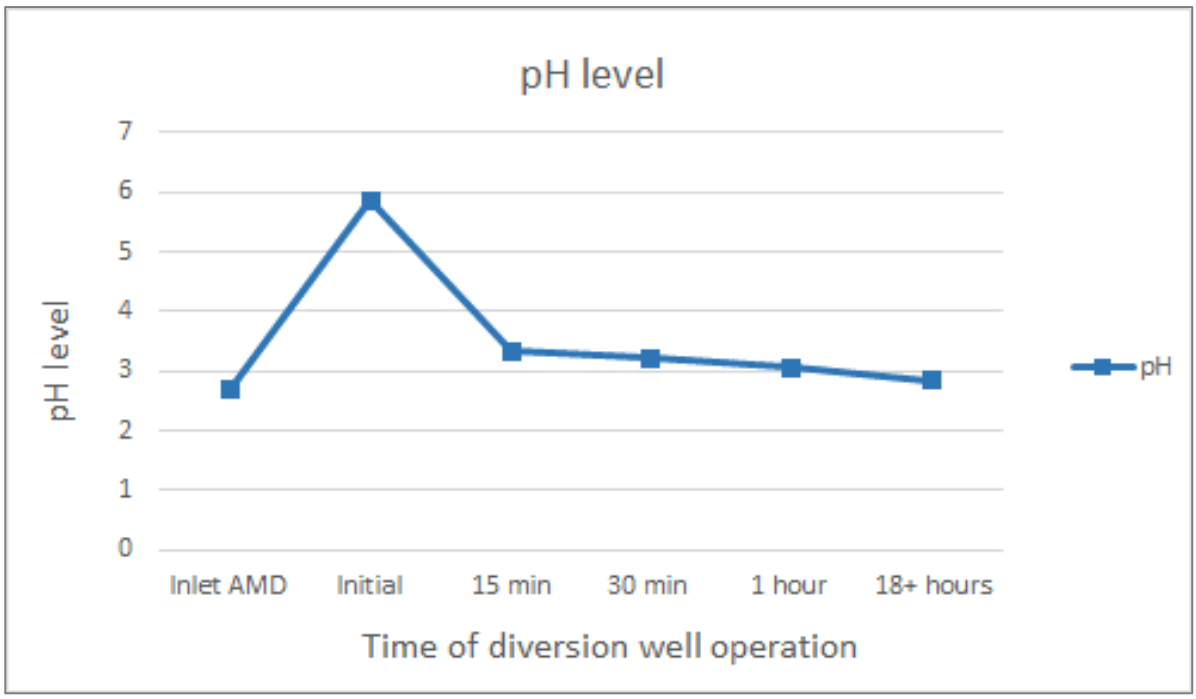

Figure 3.8 *Average pH level for inlet acid mine drainage and diversion well treated waters, using limestone substrate, over time.*

3.3.2.3 Discussion

When the acid mine drainage is first in contact with the limestone substrate (initial sampling), rapid dissolution of fine grains occurs. This produces alkalinity and raises the pH level to near neutral conditions. Metals are removed from solution either by oxidation, where metals precipitate as oxides and hydroxides, or through adsorption, where metals are concentrated on the surface area of, primarily, Fe^{3+} hydroxides. Iron hydroxides and oxyhydroxides are known to be good adsorbents of trace elements (Johnson, 1986; Hakansson, 1999). Typical precipitates include schwertmannite (iron-oxyhydroxysulfate, $Fe_8O_8(OH)_6(SO_4) \cdot nH_2O$), jarosite (potassium-iron hydrous sulfate, $KFe_3^{3+}(OH)_6(SO_4)_2$), basaluminite (hydrated aluminium sulfate, $Al_4(OH)_{10} \cdot 4H_2O$), Fe^{3+} hydroxide ($Fe(OH)_3$) and gibbsite (aluminium hydroxide $Al(OH)_3$). Al and Fe precipitate best at pH 3.5 - 4 and 6 – 7, respectively (Xinchao et al., 2005; Alintova & Petrilakova, 2011).

When the diversion well was turned on and water started flowing out the outlet, Fe and Al concentrations decrease significantly, as optimal pH levels for precipitation were reached (Figure 3.6, Figure 3.8). Mn showed little decrease in concentration over time, Ni and Zn showed no decrease. This is likely because, although pH levels were increased initially, and Al and Fe could precipitate, pH levels were still not alkali enough for Mn, Ni and Zn to precipitate out of solution. Mn usually precipitates at 9 to 9.5 pH, however, depending on the oxidation state, pH 10 is sometimes

more optimal (Alintova & Petrilakova, 2011). Ni precipitates best at pH 10 and Zn at pH 8 to 9.5 (Singh & Rawat, 1985). These pH levels were not reached and therefore, little change in Mn, Ni and Zn dissolved concentrations were seen in comparison to inlet acidic water concentrations. Previous studies show that a greater percentage of Mn and Zn are adsorbed onto Fe^{3+} hydroxides at pH 8-10 and 7-9, respectively (Millward & Moore, 2003). Adsorption is likely occurring to remove these trace metals from solution however, as optimal pH conditions are not reached, it is likely that adsorption rates are low.

The finer grained limestone dissolved to produce alkalinity in early stages of system operation therefore, over time, the dissolution rate decreased, slowing down improvements in chemistry and water quality. After 30 minutes, and especially after 18 hours, pH levels decreased again to levels similar to the inlet acid drainage (Figure 3.8). By this stage, the limestone was not dissolving as rapidly, neutral conditions were not reached and subsequently, metal contaminants could not precipitate out of solution. Optimal fluidization was not seen in the remaining substrate after 18 hours, likely because the finer grains had left the system leaving the larger, heavier grains behind which do not fluidize as easily. The limestone substrate in the diversion well system did actually prove effective, however, with the given site specific conditions and the type of diversion well set up used, effective treatment of acid mine drainage could not be achieved long term. The volume of substrate in this set up was not enough given the amount of water being treated. Greater amounts of limestone would likely make this set up more effective.

3.3.3 Mussel Shell Results

3.3.3.1 Water Chemistry

One sample was taken for each total, dissolved and sulphate analysis for each time interval (inlet acid mine drainage, initial outlet, 15 minutes, 30 minutes, 1 hour and 18 hours). This was repeated three times using mussel shell substrate over several trips to the Bellvue site. Initial sampling of treated water using mussel shell substrates showed immediate improvements in water chemistry and quality, showing similar patterns to that of limestone treatment. Initially, dissolved Al and Fe concentrations decreased, dissolved Al averaged 26.3 g/m^3 (ranged from 21 to 36 g/m^3), Fe averaged 41.07 g/m^3 (5.2 to 90 g/m^3). However, little improvement was seen with Mn, Ni and Zn. Dissolved concentrations showed little difference from inlet acid mine drainage chemistry. Mn averaged 0.7 g/m^3 (0.62 to 0.9 g/m^3), Ni averaged 0.121 g/m^3 (0.095 to 0.145 g/m^3) and Zn averaged 0.29 g/m^3 (0.22 to 0.38 g/m^3). Sulphate averaged 746.7 g/m^3 (620 to 860 g/m^3).

At 15 minutes of diversion well operation time, dissolved metal concentrations began to increase again, indicating a decrease in improvement of water chemistry over time. Dissolved Al concentrations averaged 36.5 g/m^3 (ranged from 33 to 40 g/m^3), Fe averaged 75.5 g/m^3 (51 to 100 g/m^3). Note the increase in dissolved Fe concentrations after 15 minutes are greater than inlet acid mine drainage, this is likely due to lack of data at 15-minute interval and therefore, averages appear higher than expected.

Mn, Ni and Zn again, showed little improvement from inlet acid mine drainage chemistry. Mn averaged 0.82 g/m^3 (0.71 to 0.93 g/m^3), Ni averaged 0.136 g/m^3 (0.121 to 0.151 g/m^3) and Zn averaged 0.34 g/m^3 (0.29 to 0.39 g/m^3). Sulphate averaged 780 g/m^3 (730 to 830 g/m^3).

After 30 minutes of diversion well operation, Al averaged 35 g/m^3 (ranged from 29 to 43 g/m^3), Fe averaged 64.3 g/m^3 (25 to 113 g/m^3), Mn averaged 0.74 g/m^3 (0.6 to 0.92 g/m^3), Ni averaged 0.125 g/m^3 (0.102 to 0.15 g/m^3), Zn averaged 0.31 g/m^3 (0.25 to 0.4 g/m^3) and sulphate averaged 750 g/m^3 (620 to 910).

After 1 hour of diversion well operation, Al averaged 36.3 g/m^3 (ranged from 32 to 44 g/m^3), Fe averaged 67.67 g/m^3 (29 to 119 g/m^3), Mn averaged 0.73 g/m^3 (0.6 to 0.89 g/m^3), Ni averaged 0.126 g/m^3 (0.103 to 0.155 g/m^3), Zn averaged 0.31 g/m^3 (0.24 to 0.4 g/m^3) and sulphate averaged 756.7 g/m^3 (620 to 940).

After 18 hours of treatment, dissolved metal concentrations showed no improvement in water chemistry. Some concentrations were greater than the inlet acid mine drainage, although this is not surprising, as the chemistry of the acidic drainage does fluctuate day to day, the point being that the diversion well, using a mussel shell substrate, is not effective after this length of time. Less fluidization of grains was seen after this length of time. With the finer shells having been consumed and left the well, larger heavier grains remained and were more difficult to fluidize. Also, armouring had taken place by this stage, inhibiting further dissolution. Dissolved Al averaged 39.4 g/m^3 (ranged from 30 to 55 g/m^3), Fe averaged 73.7 g/m^3 (33 to 131 g/m^3), Mn averaged 0.72 g/m^3 (0.56 -0.87 g/m^3), Ni averaged 0.127 g/m^3 (0.10 to 0.148 g/m^3), Zn averaged 0.32 g/m^3 (0.24 to 0.44 g/m^3) and sulphate averaged 770 g/m^3 (610 to 1,000 g/m^3).

Dissolved metal concentrations for diversion well treatment using a mussel shell substrate are shown in figures 3.9 and 3.10 below.

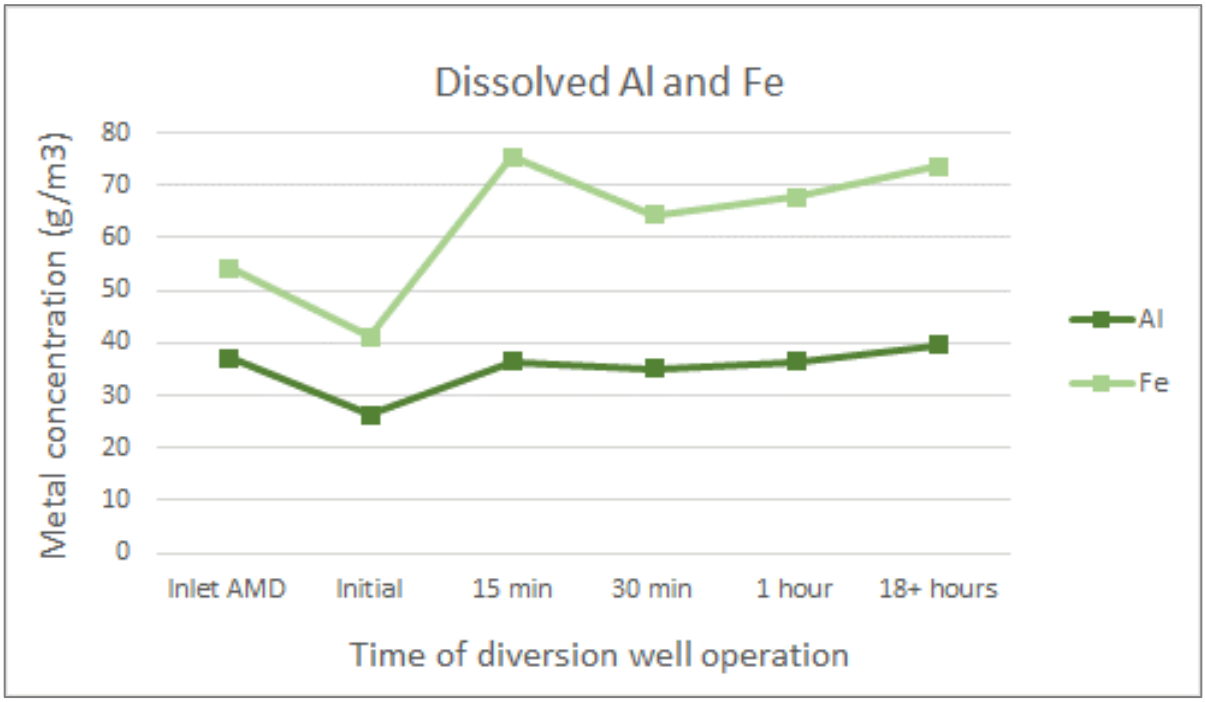

Figure 3.9 *Dissolved Al and Fe concentrations of treated waters using mussel shell substrate in a diversion well system.*

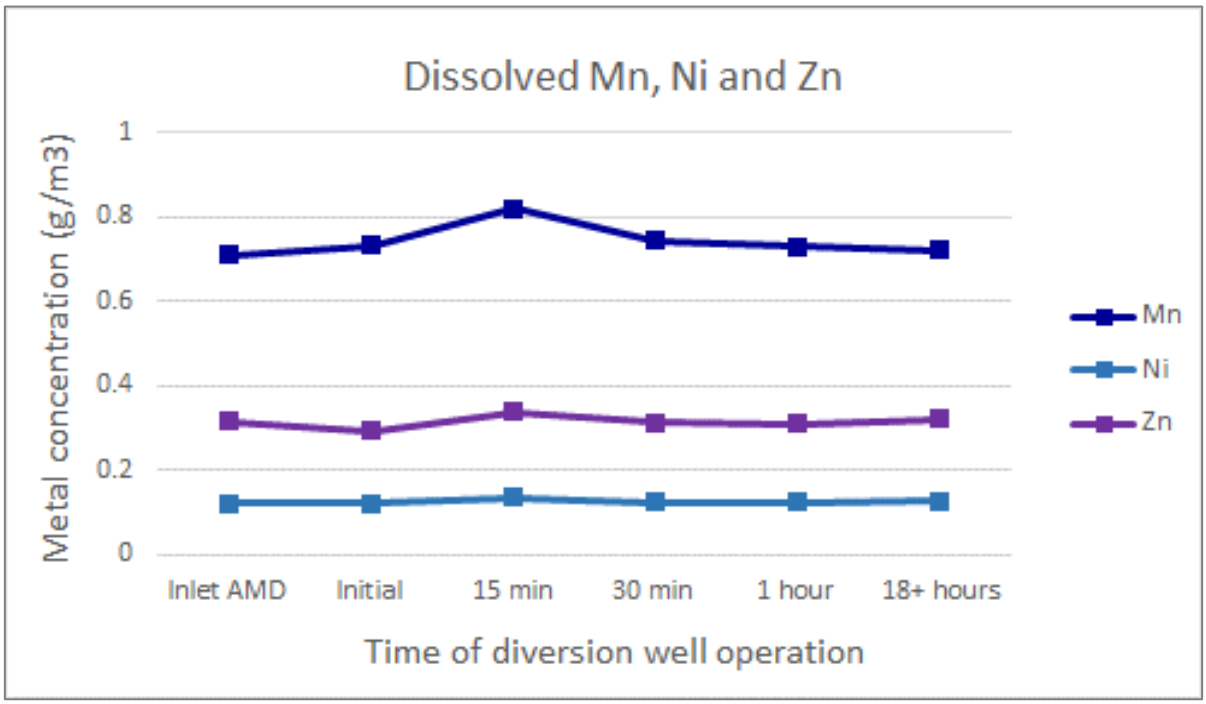

Figure 3.10 *Dissolved Mn, Ni and Zn concentrations of treated waters using mussel shell substrate in a diversion well system.*

3.3.3.2 Water Quality

Water quality data was collected using field instruments once for every time interval (inlet acid mine drainage, initial outlet, 15 minutes, 30 minutes, 1 hour and 18 hours). This was repeated three times using mussel shell substrate over several trips to the Bellvue site. Water quality parameters of treated waters using mussel shells, showed similar patterns to that of metal contaminant concentrations over time. Figure 3.11 shows averaged pH levels of treated water using shells. Immediate improvements in water quality were seen. Initially, average pH levels increased to 3.79 (ranged from 3.5 to 4.09), dissolved oxygen averaged 46.7%, electric conductivity averaged 1,411 µs/cm.

After 15 minutes of diversion well operation, pH levels began to decrease again, indicating that dissolution of shells had decreased, and production of alkalinity and subsequent neutralisation of acidic water had slowed. Average pH levels only reached 3.11 (3 to 3.25). Dissolved oxygen averaged 48.7% and electric conductivity averaged 2,030 µs/cm.

After 30 minutes of diversion well operations, even less improvement in water quality was seen. Average pH levels only reached 2.99 (2.9 to 3.06), dissolved oxygen averaged 39.35%, electric conductivity averaged 1,550 µs/cm.

After 1 hour, pH levels averaged 2.93 (2.9 to 2.97), dissolved oxygen averaged 43.8%, electric conductivity averaged 2,270 µs/cm.

After 18 hours, no improvements in water quality could be seen, pH levels only averaged 2.8 (2.68 to 2.9). Dissolved oxygen averaged 56.6% and electric conductivity averaged 2,477 µs/cm.

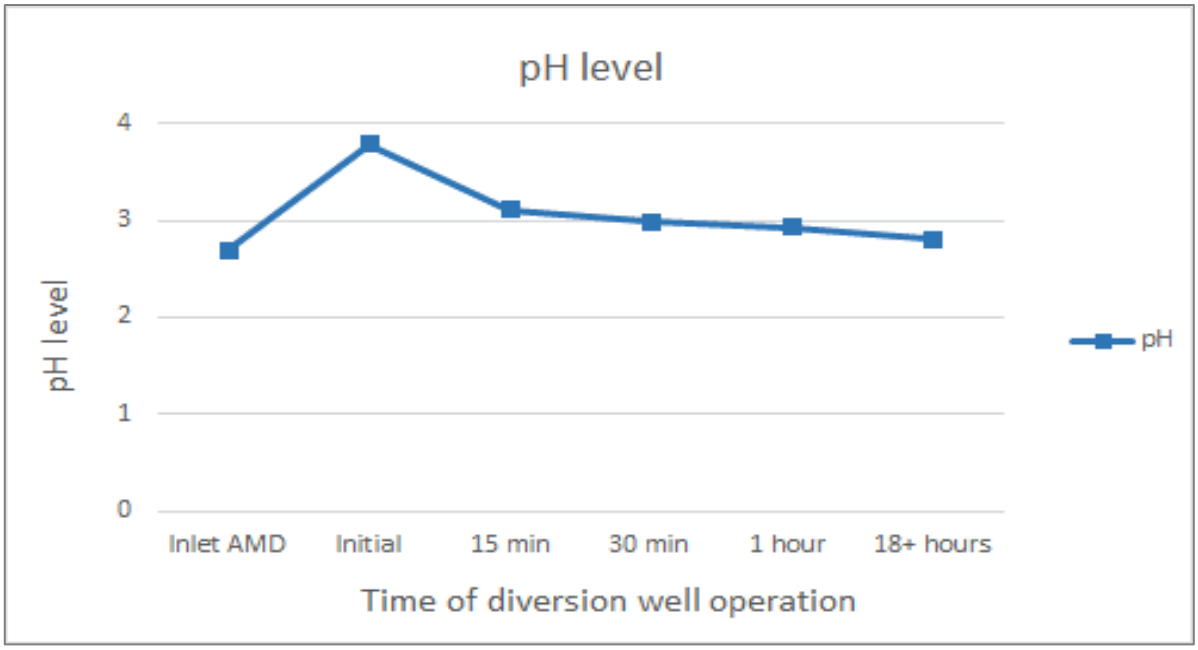

Figure 3.11 *Average pH level for inlet acid mine drainage and diversion well treated waters, using mussel shell substrate, over time.*

3.3.3.3 Discussion

Similar to trends seen with the limestone treatment, rapid dissolution of mussel shell grains occurs when the diversion well initially operates. Finer shell grains dissolve quickly and alkalinity is produced. Metal contaminants, specifically Al and Fe, precipitate out of solution, either through precipitation as oxides and hydroxides or through adsorption. However, although neutralisation still occurs, the pH level reached is not high enough to allow optimal precipitation of Mn, Ni and Zn and these metals remain in dissolved concentrations similar to that of the inlet acid mine water. Over time, finer shell grains in the diversion well are dissolved and after 15 minutes, neutralisation and production of alkalinity decreases. After 30 minutes, 1 hour and after 18 hours, the diversion well system, is no longer effective at treating acid mine drainage. Not enough dissolution of shells and subsequent alkalinity production is occurring to allow pH levels to rise enough for metals to precipitate out. Although using mussel shells in a diversion well proves some success with initial operation time, long term, it is not an effective substrate for diversion well passive treatment of acid mine drainage.

3.3.4 Comparison Between Limestone and Mussel Shells

Both substrates, as discussed in previous section, follow a similar trend in terms of effectiveness of treatment over time. With this diversion well set up at Bellvue, initially treatment works effectively, and pH levels increase, metal contaminants, specifically Al and Fe, decrease. However, the longer the diversion well system operates, the less effective at treatment this system becomes. Finer substrate grains are rapidly dissolved with initial contact with either the limestone or mussel shell, over time, finer substrate grains are consumed, and neutralisation and production of alkalinity slows down, decreasing the ability for metals to precipitate out of solution. Despite this lack of long term function, comparison of substrates can still be made. Comparing dissolved metal concentrations and water quality parameters of limestone and mussel shells will determine which substrate is more effective at treating acid mine drainage at Bellvue Mine in a diversion well set up. Metal concentrations and pH levels for both limestone and mussel shell substrates have been compared in Figures 3.12 to 3.17 below.

3.3.4.1 Comparison of Water Chemistry

Dissolved Al concentrations show a rapid decrease, for both limestone and mussel shells, with initial diversion well operation. However, treatment using the limestone substrate shows a greater decrease (0.54 g/m^3 for limestone, compared to only 26.3 g/m^3 for mussel shells). Over time, dissolved Al using limestone treatment remains in smaller concentrations than that of the shells, indicating that the limestone is a more effective treatment for removal of Al.

Similarly, with dissolved Fe, a decrease in concentrations when diversion well initially operated. Fe concentrations decreased to an average 14.9 g/m^3 using limestone, compared to an average 41.07 g/m^3 using shells. Over operation time, concentrations remain lower for limestone treatment than that of the shells. Note sudden peak in concentrations at 15 minutes of operation time, this is linked to lack of data at 15-minute interval and therefore, averages for both limestone and mussel shell treatment appear higher than expected. Lower concentrations for limestone treatment still indicate the limestone is a more effective treatment.

For dissolved Mn concentrations, mussel shells appear to have worked slightly better initially (average 0.73 g/m^3 for shells compared to 0.78 g/m^3 for limestone). However, over time, concentrations using limestone substrate showed greater decreases (0.61 g/m^3 for limestone compared to 0.72 g/m^3 for shells, after 18 hours of operation time).

Limestone treatment also is also shown to be more effective at removal of Ni from solution. Dissolved Ni concentrations for initial system operation were 0.118 g/m^3 and 0.121 g/m^3, for limestone and mussel shells, respectively. Over time, the limestone treatment showed a greater effect with concentrations for 18 hours operation time being 0.105 g/m^3 and only 0.127 g/m^3 for mussel shells.

Again, limestone treatment proves more effective with Zn removal. Initially, concentrations were 0.23 g/m^3 for limestone and 0.29 g/m^3 for mussel shells. After 18 hours of operation time, concentrations were 0.25 g/m^3 for limestone and only 0.32 g/m^3 for mussel shells.

Dissolved Mn, Ni and Zn concentrations, using both limestone and mussel shell treatment, do not vary significantly from the inlet acid mine drainage, showing little improvement in chemistry over time. This indicates this type of system set up was not allowing the increases in pH levels necessary for optimal precipitation and is therefore, not an effective treatment for removal of these trace metals. However, it is expected that there would be some removal of the metals, even at neutral pH conditions, through absorption. Little change in these metal concentrations from inlet acid mine drainage chemistry, indicates that absorption is not largely influencing metal removal. Also note similar issues with sudden peak in concentrations at 15 minute interval, linked to the lack of data and subsequent unexpected increase in average dissolved concentrations.

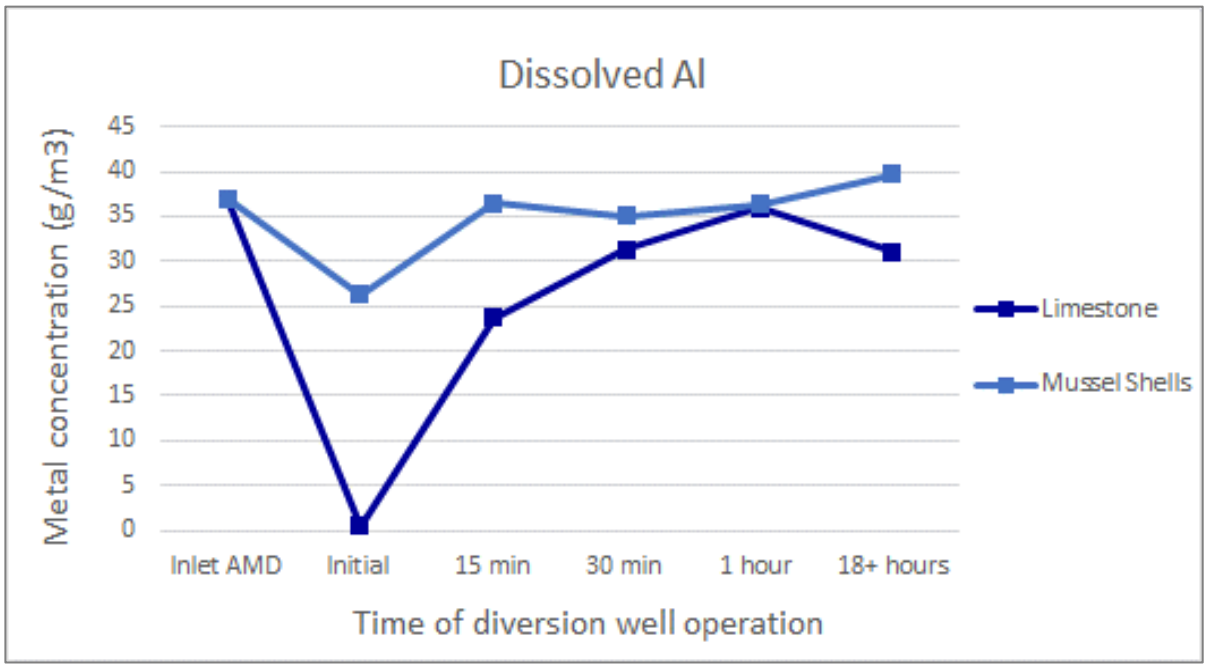

Figure 3.12 *Dissolved Al concentrations for treatment using limestone substrate in comparison to mussel shell substrate.*

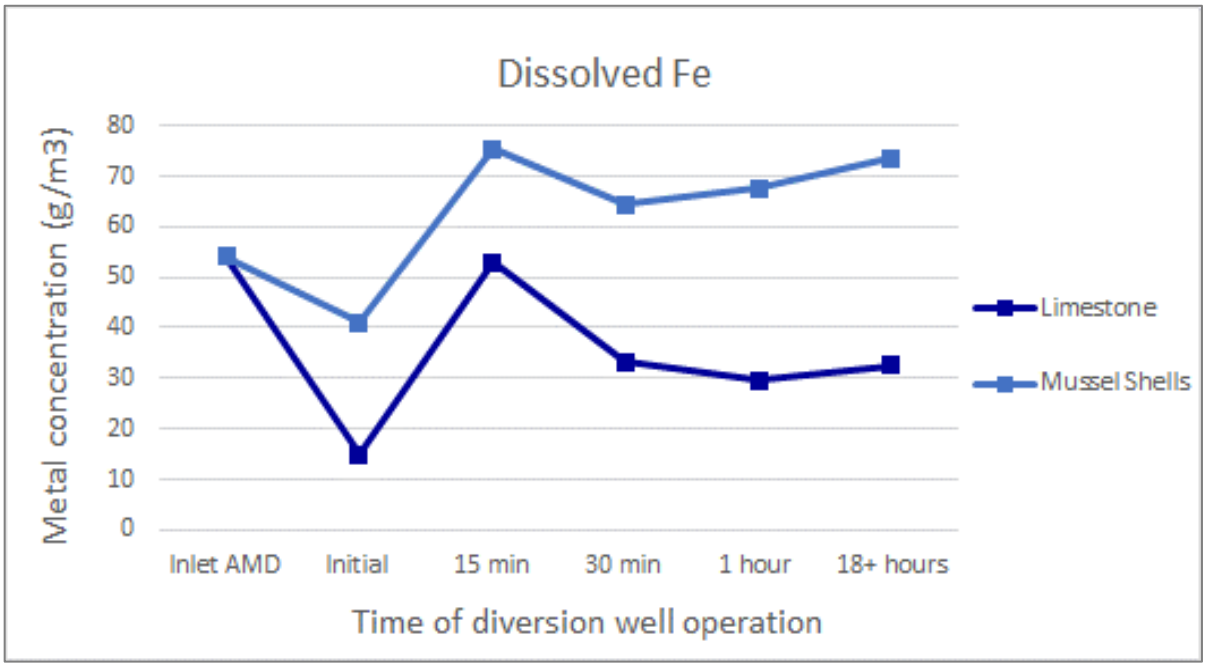

Figure 3.13 *Dissolved Fe concentrations for treatment using limestone substrate in comparison to mussel shell substrate.*

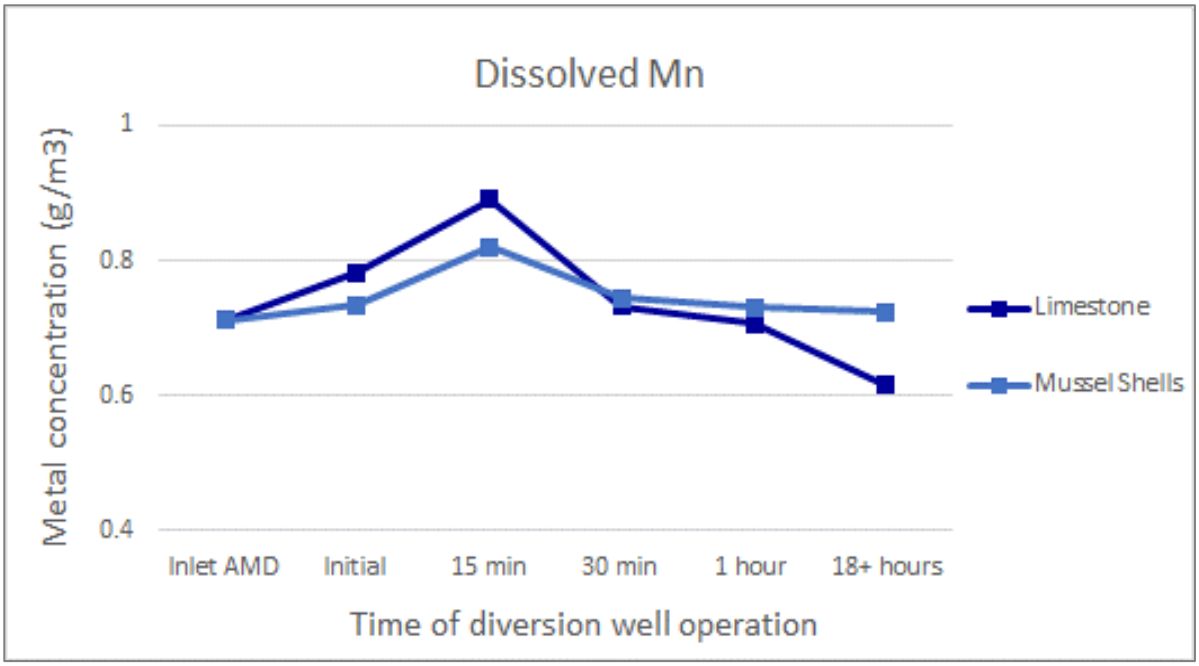

Figure 3.14 *Dissolved Mn concentrations for treatment using limestone substrate in comparison to mussel shell substrate.*

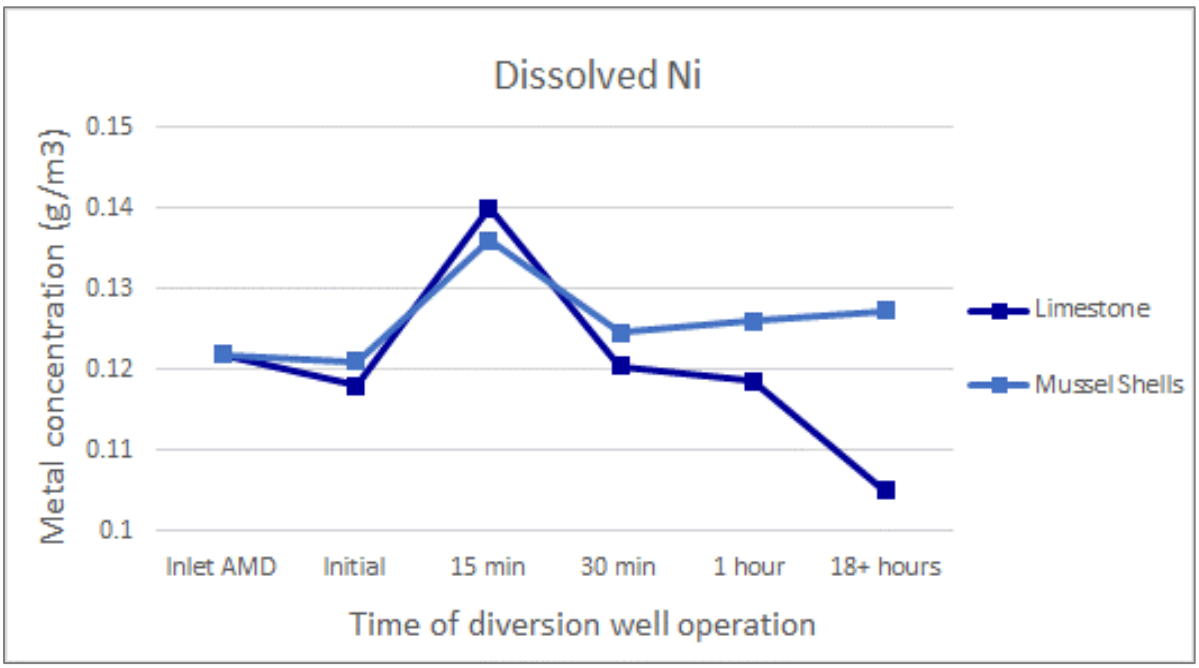

Figure 3.15 *Dissolved Ni concentrations for treatment using limestone substrate in comparison to mussel shell substrate.*

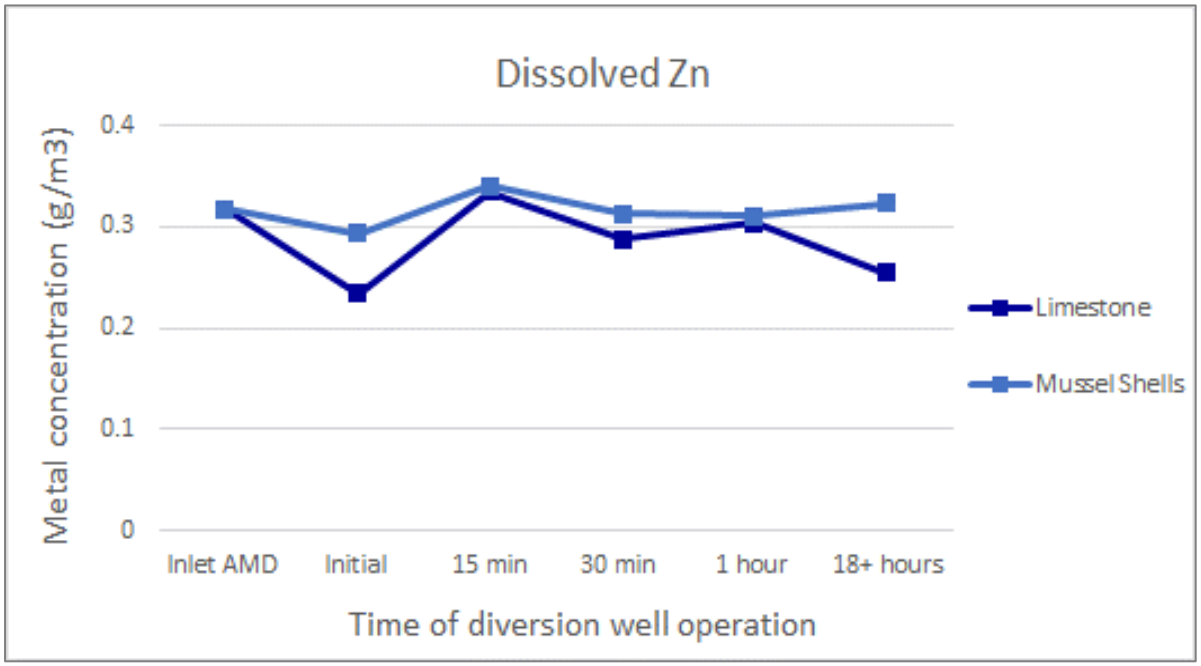

Figure 3.16 *Dissolved Zn concentrations for treatment using limestone substrate in comparison to mussel shell substrate.*

3.3.4.2 Comparison of pH Levels

Similarly, with water chemistry and dissolved metal concentrations, the limestone treatment proves more effective at raising the pH of acidic water, compared to that of the mussel shells.

With initial diversion well operation, limestone treatment increases pH levels to an average 5.86, compared to only 3.79 using the mussel shells. Over time, and throughout the course of treatment, the limestone shows greater pH levels than the shells (Figure 3.17). After 18 hours of treatment using limestone pH levels still show slightly greater averages than the shells, 2.84 compared to 2.8, respectively.

Treatment using limestone proves more effective at producing alkalinity, raising the pH and subsequently, resulting in the removal of more metal contaminants, specifically Al and Fe, from the acidic water.

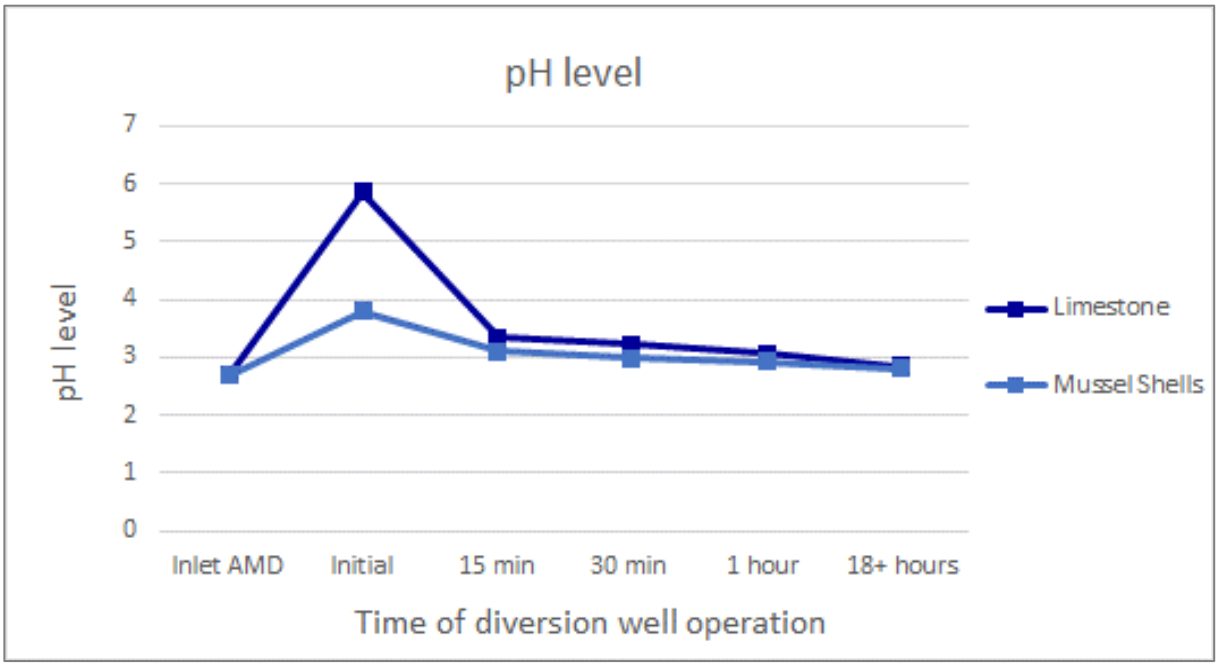

Figure 3.17 *Comparison of pH levels using limestone and mussel shell diversion well substrates.*

3.3.4.3 Discussion

Treatment using both limestone and mussel shells showed changes, and with initial operation, improvements, in water chemistry and quality. Limestone treatment however, proved to be more effective at raising the pH level of acidic waters, especially with initial diversion well operations, subsequently allowing for the removal of metal contaminants from solution. Greater decreases in dissolved metal concentrations, specifically Al and Fe, occurred using limestone as a diversion well substrate compared to the mussel shells. Greater increases in pH levels were seen with the limestone compared to the shells.

Although both substrates are comprised of the same constituent, calcium carbonate, the limestone proved more effective. The question is why is the limestone in this diversion well set up, showing to be a more effective substrate? One possible theory is the idea that shells are very hard. Designed to keep the ocean out, mussel shells remain tough and rigid and do not break down easily, compared to limestone, which can be broken apart by touching it with small force. When the shells are in contact with acidic water, although dissolution of the calcium carbonate does still occur, it is at a much slower rate due to the durability of the shells, reducing the ability for dissolution and neutralisation of mine waters. Another possible reason for the limestone being more effective is the armouring of the substrates. Armouring occurred over time with both substrates however, less coating of grains was seen with the limestone compared to the shells. The limestone grains are rough compared to the shells which have smoother surfaces. It is possible that grain to grain contact during fluidization of the rough limestone grains allows precipitates do break off, reducing this armouring effect. The smooth surface of the mussel shells likely prevents precipitates breaking off during fluidization and grain contact. Limestone is therefore, a better suited substrate for passive treatment of acid mine drainage using an oxidising diversion well system.

3.3.5 Mixed Substrate

Although the mussel shells proved to be ineffective as a diversion well substrate, compared to the limestone, a combination of both substrates was tested to determine if using the shells could still benefit in some way. One theory being that the rougher limestone grains would come into contact with the mussel shell grains, helping break down the shells into finer sized grains, aiding dissolution of both substrates. Keeping the same system parameters, 30 L of the 0-5 mm limestone and 30 L of 0-4.5 mm mussel shells were combined and tested once as a mixed substrate. Results are discussed below.

3.3.5.1 Water Chemistry

Treatment using a mixed substrate showed similar trends to that of the limestone and mussel shell substrates. Initially, treatment worked well. Dissolved Al concentrations were 3.8 g/m^3, Fe 39 g/m^3, Mn 0.75 g/m^3, Ni 0.11 g/m^3, Zn 0.25 g/m^3 and sulphate 710 g/m^3.

After 15 minutes however, improvements in chemistry decreased. Dissolved concentrations for Al were 30 g/m^3, Fe 46 g/m^3, Mn 0.71 g/m^3, Ni 0.113 g/m^3, Zn 0.26 g/m^3 and sulphate 710 g/m^3.

After 30 minutes, dissolved concentrations for Al were 33 g/m^3, Fe 54 g/m^3, Mn 0.71 g/m^3, Ni 0.112 g/m^3, Zn 0.27 g/m^3 and sulphate 700 g/m^3.

After an hour of treatment, no improvement in chemistry could be seen. Metal concentrations were similar to the inlet acid water. Al 33 g/m^3, Fe 55 g/m^3, Mn 0.69 g/m^3, Ni 0.11 g/m^3, Zn 0.27 g/m^3 and sulphate 710 g/m^3. No 18 hour sampling was carried out.

Dissolved metal concentrations are displayed in Figures 3.18 and 3.19 below.

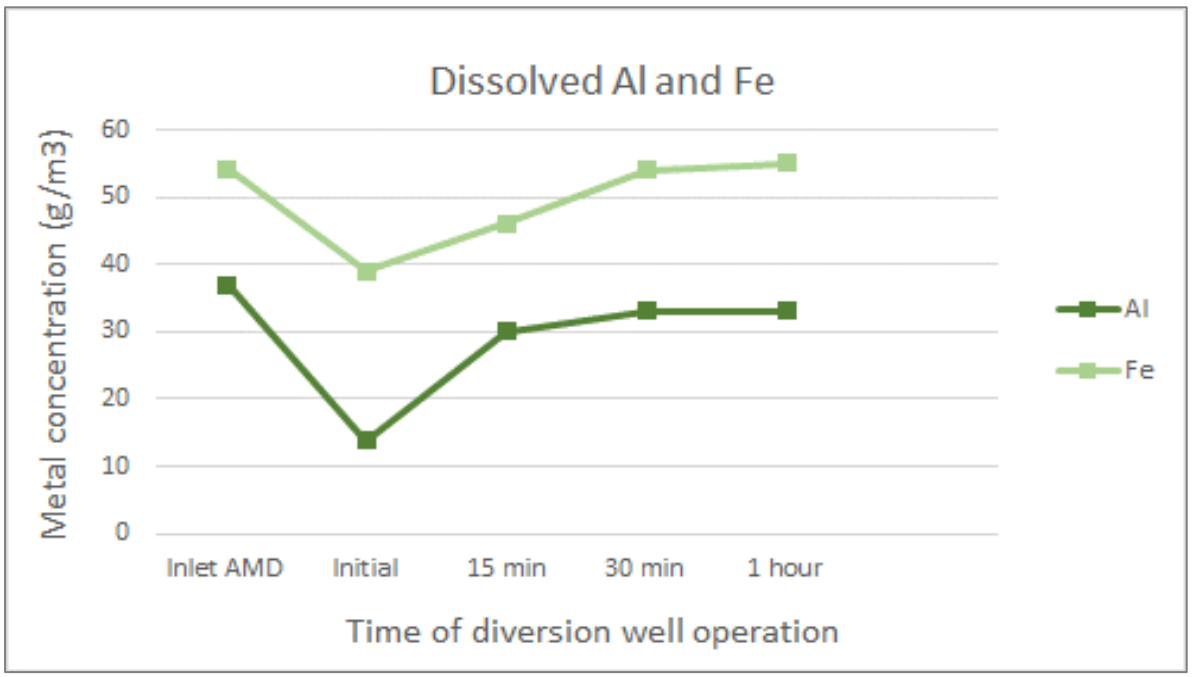

Figure 3.18 *Dissolved Al and Fe concentrations of treated waters using a mixed substrate in a diversion well system*

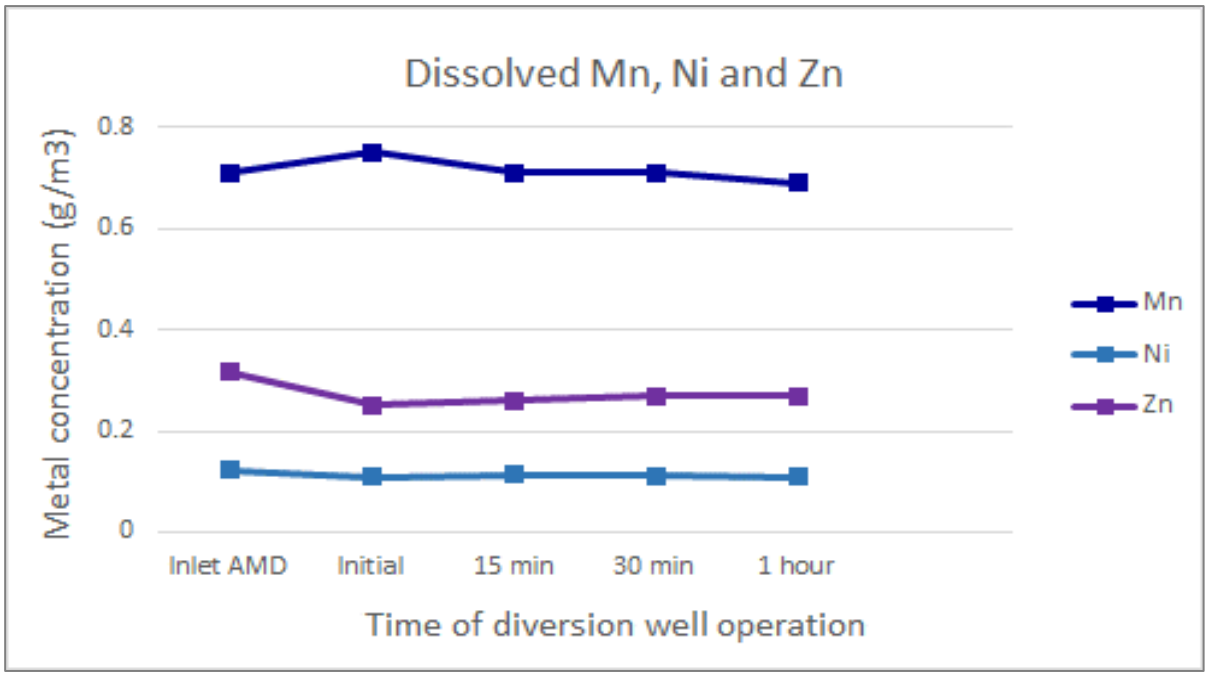

Figure 3.19 *Dissolved Mn, Ni and Zn concentrations of treated waters using a mixed substrate in a diversion well system*

3.3.5.2 Water Quality

Water quality parameters of treated waters using a mixed substrate, showed similar trends to the water chemistry results over time. Figure 3.20 shows pH level of treated water using a mixed substrate. Immediate improvements in water quality were seen. Initially, pH levels increased to 4.6, dissolved oxygen was 54.4 % and electric conductivity 1,860 µs/cm.

After 15 minutes of diversion well operation, pH levels decreased again, indicating that the dissolution rate of the substrate had decreased, subsequently decreasing neutralisation and production of alkalinity. The pH level only reached 3.6, dissolved oxygen was 47.8 % and electric conductivity 1,844 µs/cm.

After 30 minutes, improvements in water quality continued to decrease. The pH level only reached 3.2, dissolved oxygen 45.7 %, and electric conductivity 2,008 µs/cm.

After 1 hour, pH levels were 3.1, dissolved oxygen 49.8 % and electric conductivity 2,124 µs/cm.

The mixed substrate was only tested once in the diversion well system, for each time interval and therefore, only one data set can be used, averages and ranges could not be calculated. Further testing of a mixed substrate is necessary to determine more specific results.

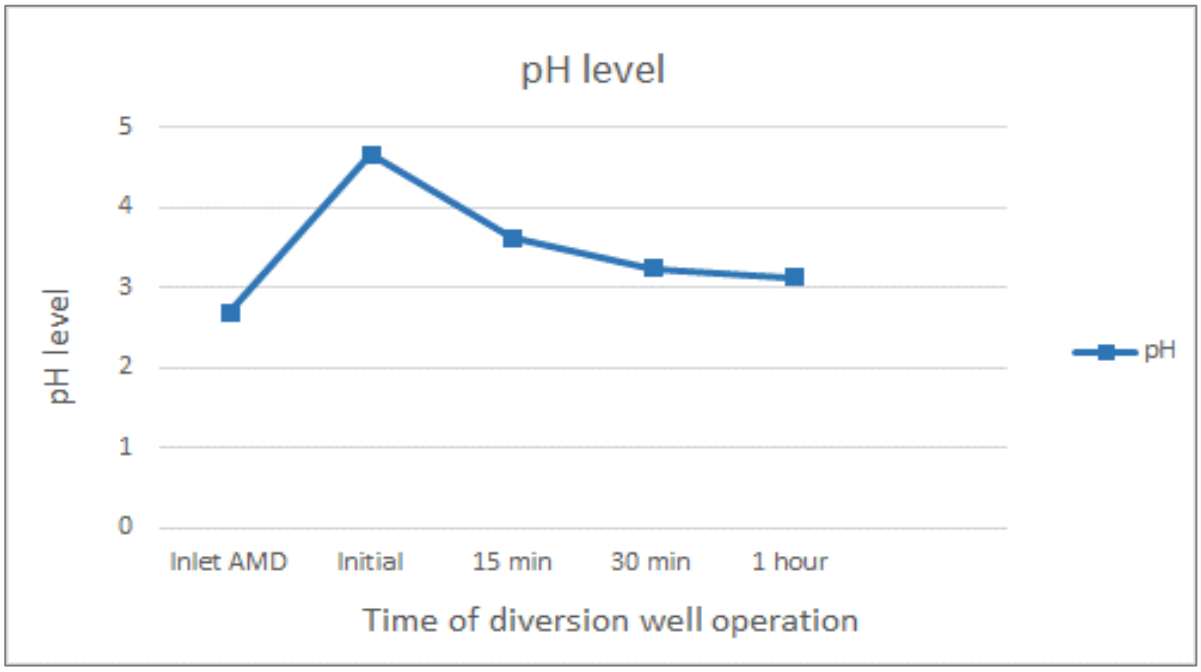

Figure 3.20 *pH level for inlet acid mine drainage and diversion well treated waters, using mixed substrate, over time.*

3.3.5.3 Comparison

Comparison between the individual limestone, mussel shells and mixed substrate can be made. Over all, the limestone worked best, followed by the mixed substrate and finally the mussel shells. Initially, dissolved Al concentrations were 0.55 g/m^3 using limestone, 13.8 g/m^3 using a mixed substrate and only 26.3 g/m^3 using mussel shells. Dissolved Fe concentrations were 15 g/m^3 for limestone, 39 g/m^3 for mixed and 41.1 g/m^3 for mussel shells. Some similar trends were seen with the dissolved Mn, Ni and Zn concentrations however, these metals in all substrate tests showed little change from inlet acidic waters and therefore, the system was not as effective for removal of these metals.

After 15 minutes, similar trends could be made, with the limestone being most effective, followed by the mixed substrate, then the mussel shells. Dissolved Al concentrations for 15 minutes were 23.7 g/m^3 for limestone, 30 g/m^3 for mixed and 36.5 g/m^3 for mussel shells. Dissolved Fe concentrations were 53 g/m^3 for limestone, 33 g/m^3 for mixed and 75.5 g/m^3 for mussel shells.

After 30 minutes, dissolved Al concentrations were 31.3 g/m^3 for limestone, 33 g/m^3 for mixed and 35 g/m^3 for mussel shells. Dissolved Fe; concentrations were 33.3 g/m^3 for limestone, 54 g/m^3 for mixed and 64.3 g/m^3 for mussel shells.

After 1-hour, dissolved Al concentrations were 36 g/m^3 for limestone, 33 g/m^3 for mixed and 36.3 g/m^3 for mussel shells. The mixed showing a greater decrease here and slightly more effective treatment after 15 minutes than the individual substrates. Dissolved Fe concentrations were 29.5 g/m^3 for limestone, 55 g/m^3 for mixed and 67.7 g/m^3 for mussel shells.

The pH levels for each treatment showed similar trends, with limestone raising the pH the most, followed by the mixed and then the mussel shells. Initially, pH levels were 5.91 for limestone, 4.66 for mixed and only 3.88 for mussel shells. After 15 minutes, pH levels were 4.17 for limestone, 3.11 for mixed and 3.13 for shells. The individual shells and mixed substrate showing very little difference in pH. After 1 hour, 3.09 for limestone, 3.13 for mixed and 2.93 for mussel shells. After this length of time, the system was no longer having a large effect on water chemistry and quality, all substrates showed little increase in pH.

No data was collected after 18 hours for mixed substrate tests. Only one sample was taken for time interval; initial, 15 minutes, 30 minutes and 1 hour, for only one test using the mixed substrate. Therefore, more data collection and testing using the mixed substrate would be necessary for more accurate comparison of substrates. The mixed does prove to be more effective than the mussel shells alone. Looking forward and at future research, it is possible a mixed substrate in this type of passive treatment system could be a way of reducing the cost of using a limestone only substrate.

3.3.5.4 Discussion

Initial water chemistry and quality improved with treatment using the mixed substrate. Dissolution of the finer grained limestone and mussel shells allowed rapid production of alkalinity and thus, raised the pH level to near neutral conditions, where Al and Fe could start to precipitate. However, the pH level was still not great enough to allow optimal precipitation of Mn, Ni and Zn. The concentrations of these metals therefore, remained similar to that of the inlet acid mine drainage chemistry. After 15 minutes of operation time, water chemistry and quality began to decrease. The fine substrates had likely been dissolved already and dissolution rates slowed. The pH level did not

reach optimal levels for metal removal. After 30 minutes and 1 hour, chemistry and water quality showed very little improvements. Similarly, with the individual limestone and mussel shell treatment, the mixed substrate treatment showed lack of ability to function effectively over time. The mixed substrate was more effective at treatment of acid mine drainage compared to the individual mussel shells however, showed to be less effective than the limestone.

3.4 Summary

A diversion well system was set up at Bellvue Mine site, based on results of fluidization experiments and given site conditions. A 110 L barrel was used as the well and was linked to two IBC's. This increased residence time, allowing time for further calcium carbonate dissolution and subsequent neutralisation reactions to occur. Acid mine drainage was siphoned from pooled mine water at the mine adit into the well and down over the substrate. Water then flowed vertically up through the substrate and was piped from the well into IBC 1 and 2 consecutively. Treated outlet water then flowed out of IBC 2 and into Cannel Creek. Limestone, mussel shells and a mixed of both were tested as diversion well substrates individually, over several trips to the site. Sampling and chemical analysis was carried out (total and dissolved Al, Fe, Mn, Ni, and Zn and sulphates) and water quality parameters (pH level, electric conductivity and dissolved oxygen) were measured to determine which substrate was more effective at treatment of acid mine drainage at Bellvue.

Treatment using the limestone substrate showed improvements in water chemistry and quality immediately. Initially, decreases in dissolved metal concentrations were seen and the pH level was raised to near neutral conditions allowing precipitation of metal contaminants. However, after 15 minutes of diversion well operation time, improvements in chemistry and water quality started to decrease. Dissolved metal concentrations showed less decrease and pH levels were not increased to near neutral conditions. Similarly, with the 30 minutes, 1 hour and 18 hours of operation time, improvements in chemistry continued to decrease. This is likely a result of the finer grained limestone being consumed in early stages of operation. The fine material was easily broken down and dissolved allowing rapid neutralisation of the water. Over time, the finer material had been consumed and the remaining substrate was larger, and therefore could not be fluidized as easily resulting in armouring. This armouring inhibiting dissolution of the calcium carbonate.

Treatment using the mussel shells showed similar trends. Improvements in water chemistry and quality were seen with initial treatment. After 15 minutes of operation, improvements started to decrease. Dissolved metal concentrations showed less decrease and pH levels were not reaching

near neutral levels. With increasing diversion well operation time, improvements in water chemistry and quality decreased. Again, this is linked to the rapid consumption of the finer grains during original operation. Optimal fluidization of grains was not occurring over time and larger grains were harder to fluidize given the flow rates. This allowed for armouring of the shells, preventing further dissolution and subsequent neutralisation reactions.

The mussel shells were not as effective compared to the limestone. Treatment using limestone showed greater decreases in dissolved metal concentrations and larger increases in pH levels. This is likely because limestone is much softer than the shells and easier for the acidic water to dissolve. Also, the shells flat hard surface likely encouraged iron precipitation, compared to the limestone which had a rough surface which, when grain to grain contact occurred, could break more easily, discouraging the armouring of precipitates and allowing effective treatment for greater lengths of time. The mixed substrate did prove to be more effective than the mussel shells however, the limestone was still more effective than the mixed.

The main issue with this setup was the fact that neither of the substrate treatments were effective long term. Although having the IBCs increase residence time, the size of the well and the amount of substrate that was used was simply not enough to withstand long term treatment. More substrate is needed to allow for dissolution and neutralisation for longer periods of time. This links back to the fluidization mechanics of a diversion well system. Having more substrate in the diversion well would have prevented optimal fluidization, armouring would have occurred more quickly and although more substrate would be available for dissolution, this armouring would prevent reactions earlier on in operation.

Several main conclusions can be made from this experiment:

- The limestone is the most effective substrate for the treatment of acid mine drainage at Bellvue.
- The mixed substrate performed better than the mussel shells but not as well as the limestone.
- Initial treatment using each substrate showed improvements in water chemistry and quality, especially the limestone treatment.
- The amount of substrate was not enough to allow for long term effect treatment of acid mine drainage.

4

Limitations, Issues and Options

4.1 Overview

The main objective of this research was to trial the efficiency of a diversion well at Bellvue Mine for the treatment of acid mine drainage, at the same time, comparing the operation of a diversion well using limestone to that of mussel shells.

The operation of a diversion well at Bellvue is more complex than first anticipated. This chapter discusses some of the issues associated with diversion well set up and function at Bellvue and gives an overview on future research necessary for long term operation at the site.

4.2 Limitations and Issues at the Site

4.2.1 Long Term Diversion Well Function

Several different combinations of parameters (for example; flow rates, well diameter and height, substrate grain sizes), are necessary to achieve optimal fluidization of substrate grains. Having grains fluidize reduces the effect of armouring, the coating of substrate grains in precipitated iron hydroxides. The diversion well set up at Bellvue allowed fluidization of grains. Dissolution of calcium carbonate and subsequent neutralization of acidic water did occur. However, the size of the well was not large enough to hold the amount of substrate necessary to allow long term treatment of acid mine drainage. Having a larger diameter well (400 mm well was used) would have reduced the ability for grains nearer the outer edges of the well to fluidize, with the given flow rates at the site (averaged 2.4 L/sec). Therefore, the system only worked effectively initially. After 15 minutes of operation time, the very fine grained substrates had been consumed. Any larger grains left in the well were not able to dissolve rapidly, reducing the rate of neutralisation reactions over time. This problem occurred using both the limestone and the mussel shells, indicating an issue with diversion well function rather than chemical issues with substrate performance. Using a larger well and therefore more substrate, would increase the length of time of effective treatment. However, a

larger well diameter would decrease the fluidization ability of grains in the well, leading to armouring of substrate in early stages of operation, preventing dissolution of grains. Using a larger diameter well but also using a smaller grain size substrate may overcome this problem. Also, a system with a small diameter but large height, or cone shaped well, might improve this issue; allowing for more substrate but still allowing for optimal fluidization of grains.

4.2.2 Armouring Effect

The 'armouring' of substrate grains has been a significant issue in terms of passive treatment of acid mine drainage globally. When dissolution of calcium carbonate and subsequent production of alkalinity takes place, pH levels increase, and metal contaminants precipitate out of solution. These precipitates, specifically Fe hydroxide, coat the outer layer of substrate grains, reducing the substrate surface area and preventing further reaction between the calcium carbonate and the acidic water (Sun et al., 2000). In a diversion well system, fluidization allows grain to grain contact, as the substrates move throughout the well. This encourages the removal of these coated precipitates.

At Bellvue, the diversion well system initially had good fluidization. The size of the well, amount of substrate and given flow rates, allowed fluidization of grains to occur. However, over time, the finer grains (< 3 mm) were consumed or had left the well, leaving heavier grains behind. These grains were harder to fluidize and after several hours of operation, Fe precipitates begun to coat the remaining grains. With less fluidization, less dissolution and subsequent production of alkalinity could occur. Thus, reducing effective function of the system long term. Figure 4.1 shows some of the mussel shell substrate armoured in precipitated Fe.

Figure 4.1 *Precipitated Fe hydroxides armouring some of the mussel shell substrate after several hours of operation. Pen for scale.*

4.2.3 Crushing Mussel Shell Substrate

Passive treatment of acid mine drainage are methods designed to be of low cost, require little or no dosing of chemical agents and take advantage of the natural occurring processes at the mine site. The idea of using mussel shells as an alternate source of calcium carbonate in a diversion well system is primarily to reduce the cost of treatment. Mussel shells are a waste product of New Zealand's fishing industries and therefore, involve minimal cost to acquire.

In terms of this project, mussel shells were easily obtained as a waste product, requiring no cost. However, in order for the shells to fluidize in the diversion well, the shells needed to be crushed to less than 4.5 mm. The shells were crushed using a garden mulcher and sieved to size. This step in the process meant that it was no longer more efficient to use shells than limestone. Using crushed shells on a larger scale in a similar set up, would require cost to crush the shells pre-treatment, potentially making limestone a more desirable substrate for use in a diversion well system.

4.2.4 Diversion Well in Series

The size of the diversion well in this project, limited the amount of substrate that could be used to neutralise acid mine drainage. The more substrate available for neutralisation reactions, essentially, the longer the system can work effectively. To increase the amount of substrate used in this project set up, a diversion well in series was installed and tested. This involved having acidic drainage flowing into the first well, flow through the substrate, out of well one and into well two. The main idea being to increase the amount of substrate by having more wells and to increase the residence time of water in the system and thus time for neutralisation reactions to occur. Figure 4.2 shows how this system was set up.

This setup however, did not function effectively. There was a lack of sufficient vertical drop between the wells. The flow rate of the water flowing out of well one was suddenly reduced because of this lack of gradient. The substrate in well two, and with the reduced flow rate, prevented continuous water flow through the system. There was also not enough flow or pressure to fluidize the substrate grains in well two. Water backed up the system and ended up over flowing the top of well one. A diversion well set up in series was therefore, not used for the substrate treatment tests.

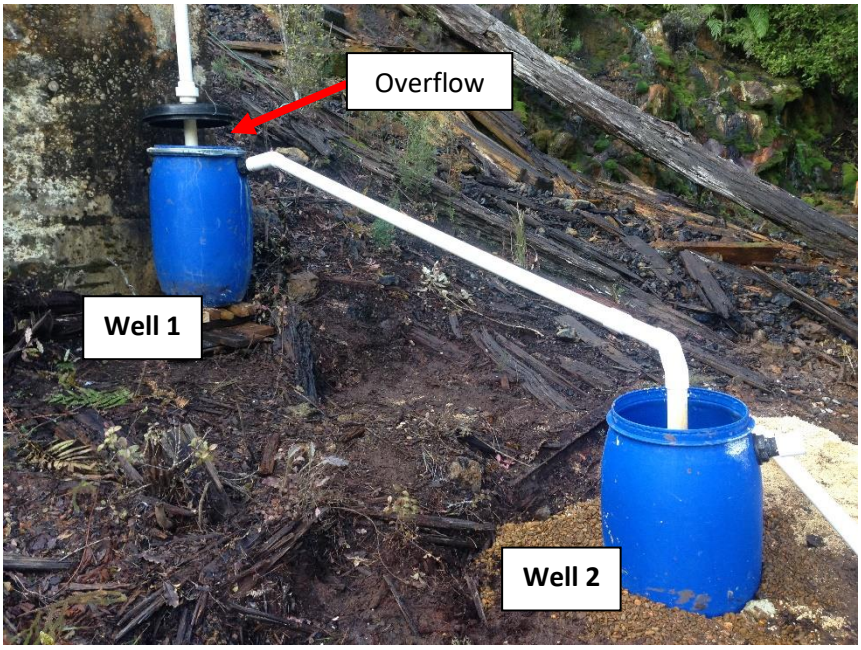

Figure 4.2 *Diversion well set up in series to increase the amount of substrate and residence time. This was not effective due to lack of vertical drop and subsequent reduction in flow rate between each well, preventing water flow through whole system, resulted in overflow of well one.*

4.2.5 Options and Future Research at Bellvue

As well as comparing the efficiency of mussel shells to that of limestone in a diversion well system, this research has aided in the understanding of the mechanisms and parameters necessary for diversion well operation at Bellvue. Future work involving larger scale treatment, would need to involve increasing the height and therefore, volume of the well, to allow for the use of more substrate and thus longevity in treatment. A larger well diameter, a residence time longer than 10 minutes, with given flow rates of 2.4 L/sec and a limestone substrate less than 5 mm in size, with a larger percentage of that substrate being less than 3 mm, is necessary to achieve a more successful setup at Bellvue. Limestone is the more desirable substrate for the most effective treatment in this type of passive treatment system.

5

Summary and Conclusions

5.1 Project Objectives

Bellvue Mine, an abandoned mine north of Greymouth, West Coast, is discharging acidic run-off into nearby Cannel Creek. This has resulted in low pH conditions and high dissolved metal concentrations subsequently having adverse effects on stream ecosystem health and water quality.

A diversion well is a form of passive treatment of acid mine drainage. This research aimed to test the efficiency of a diversion well at Bellvue, at the same time, compare the operation of a diversion well using limestone substrate to that of mussel shells.

5.2 Diversion Well Mechanics

Diversion wells operate on the basis on fluidization of substrate, to prevent armouring as metals precipitate out of solution. Achieving optimal fluidization in a diversion well system involves having the substrate fluidize the full diameter of the well and substantial percentage of the height of the well, without the substrate being flushed out. Variables which influence this are the mechanics of the well set-up such as flow rates of water flowing into the well, the inlet pipe diameter, well height and diameter and substrate type and grain size.

An experimental set up tested several different combinations of these parameters to determine what parameters were necessary for successful diversion well operation at Bellvue. Several findings were made:

- Flow rates increased as inlet pipe diameter increased. Pipe sizes less than 32 mm restricted flow rates.
- Optimal fluidization occurred with inlet pipe diameters 32 – 50 mm.
- The greater the well height, the more substrate the well can contain, the more space for fluidization. Substrates < 12 mm were being flushed out of the well with pipe sizes 32 – 50

mm and flow rates of 1 to 1.6 L/sec, indicating a greater well height could be used and fluidization would still occur.

- The larger the well diameter, the less horizontal fluidization occurred (fluidization diameter).
- Optimal fluidization occurred with 2.36 – 10 mm limestone and 4.5 – 12 mm mussel shells.

5.3 Diversion Well Passive Treatment

A diversion well system was installed at Bellvue. The set up consisted of having a barrel, the well, linked to two IBC's in series. Acid water was siphoned from pooled mine waters at the mine adit into the well and into the substrate where contact with calcium carbonate allowed neutralisation reactions to start occurring. Water then flowed consecutively into each IBC; this increased residence time and allowed for further dissolution of grains and subsequent neutralisation of acid water. Treated water flowed out IBC 2 into Cannel Creek. Limestone and mussel shells were tested separately. Chemical analysis and water quality data was collected to determine which substrate was more effective in the treatment of acid mine drainage.

Treatment using the limestone substrate showed improvements in water chemistry and quality immediately. Initially, pH levels increased rapidly to near neutral conditions and metal contaminants, specifically Al and Fe, precipitated out of solution. After 15 minutes, 30 minutes and 1 hour of diversion well operation, improvements in water chemistry and quality decreased. The pH level was not reaching neutral conditions and therefore, metal contaminants could not precipitate. After 18 hours of operation, very minimal improvement was seen. The finer grained limestone, on initial contact with the acid mine drainage, was dissolved rapidly. This allowed sudden improvements in chemistry and water quality. Over time, these finer limestone grains had been consumed, dissolved to produce alkalinity in the system. The larger grains were not dissolving as rapidly and therefore, dissolution rates and production of alkalinity in the system slowed. Although treatment using the limestone substrate did work, this meant that long term, the diversion well system was not effective at treatment of acid mine drainage.

Similar trends were seen with the mussel shell substrate. Initially, improvements in chemistry and water quality were seen. The pH level increased, and metals precipitated out of solution. However, over time finer grained shells had been consumed and dissolution rates and neutralisation reactions in the system slowed, preventing rapid increases in pH and metal removal. After 18 hours, no

improvements in chemistry and water quality were seen. The treatment using the shells did initially work however, long term effective treatment could not be achieved.

Comparison between the efficiency of the limestone and mussel shells was made. Although treatment using each substrate showed similar trends over operation time, the limestone showed greater improvements in water chemistry and quality than the mussel shells. A greater decrease in dissolved metal concentrations was seen with the limestone compared to the shells. Even after 18 hours of operation, metal concentrations were lower with limestone treatment. With initial diversion well operation, limestone treatment increased pH levels to an average 5.9, compared to only 3.9 using the mussel shells. After 18 hours of operation, limestone treatment still showed greater averages in pH level than the shells, 2.86 and 2.81, respectively. The limestone therefore, proving to be a more effective substrate in a diversion well for the treatment of acid mine drainage.

A mix of both limestone and mussel shells was also tested as a substrate in this diversion well system. The mixed substrate showed to be more effective than the shells but less so than the limestone, making the limestone the more desirable substrate for this type of passive treatment. However, only one trial of mixed substrate was tested in the system during one visit to the site. Therefore, in future, this would need to be repeated several times to get a more accurate representation of how the mixed substrate compares to the individual limestone and mussel shells.

5.3.1 Main Conclusions

Several main conclusions from this study at Bellvue can be made:

- Initial operation of the diversion well allowed effective improvement in water chemistry and quality, with both limestone and mussel shell substrates and with the mixed substrate.
- Long term effective treatment with this type of passive treatment setup could not be achieved because the well was too small to hold the sufficient amount of substrate.
- Limestone proves to be more effective at treatment of acid mine drainage in a diversion well system at Bellvue, compared to the mussel shells.

5.4 Limitations, Issue and Options

The operation of a diversion well at Bellvue was more complex than first anticipated. Several limitations and issues arose, making effective long-term treatment difficult to achieve.

The main downfall to this research was that the diversion well setup was not effective for long periods of time. With each substrate, more so with the limestone, treatment was effective with initial diversion well operation. Over time, improvements in chemistry and water quality decreased. This is primarily a result of not having a system large enough to hold the amount of substrate necessary for long term treatment. Simply put, more limestone is needed for longer dissolution and subsequent neutralisation of acidic water. However, having a larger diameter well to hold more substrate, reduces the ability to achieve optimal fluidization. Grains that are not fluidized quickly become armoured in precipitated iron hydroxides, preventing further dissolution. Future use of a diversion well at Bellvue needs to focus on increasing the height of the well and thus volume, rather than increasing diameter.

Armouring was also a significant issue with experiments at Bellvue. The size of the well, substrate grain size and given flow rates allowed optimal fluidization initially. However, over time, as fine grains had dissolved and been consumed, larger grains remained in the well. These remaining larger grains were harder to fluidize and therefore, armouring occurred, preventing further dissolution and neutralisation reactions and thus long term effective treatment.

Crushing the mussel shells became a limitation of this project. The idea behind using mussel shells for acid mine drainage treatment being shells are a waste product and are of low cost and easily accessible, are perfect for use in passive treatment. However, the shells needed to be crushed in order to achieve fluidization within the well. On a large scale, this increases the cost involved in pre-treatment, making limestone a potentially more desirable substrate.

A diversion well in series was trialled at the site in attempts to increase amount of substrate in the system and residence times. This was unsuccessful as the gradient between the wells so was not great enough to create enough hydraulic head to allow full water flow through the system. Water ended up backing up and over flowing the first well.

5.5 Future Research

The aim of this project was to compare the use of mussel shells in a diversion well system to that of limestone, for the treatment of acid mine drainage at Bellvue Mine. The results can be used to further increase knowledge and understanding of diversion well systems and the way in which these

can be utilized at mine sites in New Zealand and globally. Although the use of limestone in a diversion well still proves to be a more effective treatment, this study helps understand the mechanisms behind diversion well function and the parameters necessary for successful operation of a larger scale diversion well at the Bellvue site.

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Appendices

Appendix A

Figure 6.1 *Photo of Bellvue Mine site looking up the mine cascade, covered in old mine debris. The mine adit and pooled mine water are at the top of the cascade.*

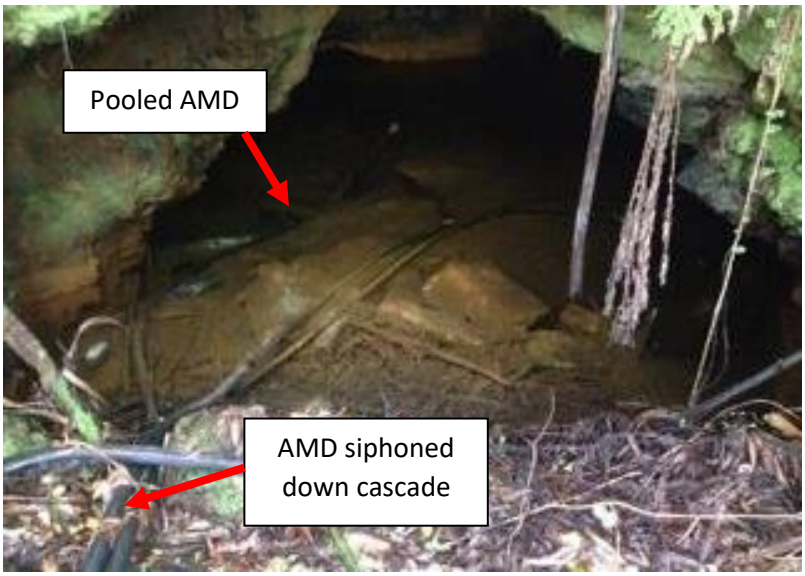

Figure 6.2 *Mine adit with pooled mine waters. Black pipes are siphoning acid mine drainage down the cascade to the diversion well set up.*

Figure 6.3 *Water flow into Cannel Creek from mine. Water flows from mine pool, down cascade and over the road into Cannel Creek. Orange appearance of the water is the Fe hydroxides, precipitated as acid mine drainage encounters neutral waters coming from upstream.*

Appendix B

Below is the raw data collected during the fluidization experiments (chapter 2). This data was used to compare mean flow rates, height and diameter of fluidized grains, to that of the inlet pipe diameter. Results then gave an idea of what parameters of a diversion well were necessary to achieve optimal fluidization results at the Bellvue Site.

Note:

\+ Indicates value would have been greater but maximum well height or diameter was reached.

x Indicates no data collected.

Well 1

			Limestone			Mussel Shells		
			AgLime	2.36-5mm	5-10 mm	4-12mm	Whole/broken	Mean Flow Rate
	Inlet Pipe Diameter							
Well 1 (blue bucket)	15 mm	*Flow rate L/sec*	0.79	0.8	0.63	0.26	0.25	0.546
		Height (mm)	120	130	0	0	0	
		Diameter (mm)	150	25	0	0	0	
	20 mm	*Flow Rate (L/sec)*	1.27	1.33	1.08	0.32	1.26	1.052
		Height (mm)	250	150	0	0	0	
		Diameter (mm)	70	30	0	0	0	
	25 mm	*Flow Rate (L/sec)*	1.44	1.65	1.77	2.13	0.79	1.556
		Height (mm)	240	150	0	180	0	
		Diameter (mm)	120	30	0	40	0	
	32 mm	*Flow Rate (L/sec)*	1.45	1.66	1.53	1.55	1.61	1.56
		Height (mm)	490+	470	0	490+	0	
		Diameter (mm)	120	50	0	110	0	
	40 mm	*Flow Rate (L/sec)*	1.56	1.6	1.53	1.51	1.63	1.566
		Height (mm)	490+	470	0	490+	0	
		Diameter (mm)	310+	60	0	130	0	
	50 mm	*Flow Rate (L/sec)*	1.56	1.65	1.58	1.53	1.6	1.584
		Height (mm)	490+	230	0	490+	0	
		Diameter (mm)	230	60	0	60	0	
	80 mm	*Flow Rate (L/sec)*	1.56	1.53	1.67	1.52	1.55	1.566
		Height (mm)	490+	230	0	180	0	
		Diameter (mm)	120	90	0	90	0	

Well 2

			Limestone			Mussel Shells		
			AgLime	2.36-5mm	5-10 mm	4-12mm	Whole/broken	Mean Flow Rate
	Inlet Pipe Diameter							
Well 2 (Grey bucket)	15 mm	*Flow rate L/sec*	0.61	0.6	0.51	0.43	0.53	0.536
		Height (mm)	530+	0	0	0	0	
		Diameter (mm)	200+	0	0	0	0	
	20 mm	*Flow Rate (L/sec)*	x	1.02	0.64	x	0.66	0.773
		Height (mm)	530+	240	0	180	0	
		Diameter (mm)	200+	200+	0	90	0	
	25 mm	*Flow Rate (L/sec)*	1.39	1.49	1.22	1.24	0.87	1.242
		Height (mm)	530+	230	150	530+	0	
		Diameter (mm)	200+	200+	140	180	0	
	32 mm	*Flow Rate (L/sec)*	1.31	1.24	1.16	0.71	0.93	1.07
		Height (mm)	530+	530+	530+	530+	0	
		Diameter (mm)	200+	200+	140	200+	0	
	40 mm	*Flow Rate (L/sec)*	1.3	1.26	1.22	x	1.23	1.2525
		Height (mm)	530+	530+	530+	530+	0	
		Diameter (mm)	200+	200+	110	200+	0	
	50 mm	*Flow Rate (L/sec)*	1.26	1.24	x	1.19	1.39	1.27
		Height (mm)	530+	530+	530+	530+	0	
		Diameter (mm)	200+	200+	80	180	0	
	80 mm	*Flow Rate (L/sec)*	1.26	1.38	1.41	1.36	1.28	1.338
		Height (mm)	530+	530+	530+	530+	0	
		Diameter (mm)	200+	200+	80	130	0	

Well 3

			Limestone			Mussel Shells		
			AgLime	2.36-5mm	5-10 mm	4-12mm	Whole/broken	Mean Flow Rate
	Inlet Pipe Diameter							
Well 3 (White 5 L bucket)	15 mm	*Flow rate L/sec*	0.9	0.84	0.83	0.83	0.85	0.85
		Height (mm)	250+	80	0	80	0	
		Diameter (mm)	190+	160	0	20	0	
	20 mm	*Flow Rate (L/sec)*	1.48	1.28	1.05	1.22	1.25	1.256
		Height (mm)	250+	250+	90	250+	0	
		Diameter (mm)	190+	190	70	90	0	
	25 mm	*Flow Rate (L/sec)*	x	1.42	1.25	1.38	1.43	1.37
		Height (mm)	250+	250+	125	250+	0	
		Diameter (mm)	190+	190+	95	190+	0	
	32 mm	*Flow Rate (L/sec)*	1.48	1.37	1.32	1.43	1.49	1.418
		Height (mm)	250+	250+	250+	250+	250+	
		Diameter (mm)	190+	190+	170	190+	150	
	40 mm	*Flow Rate (L/sec)*	1.53	1.3	1.37	1.42	1.48	1.42
		Height (mm)	250+	250+	250+	250+	120	
		Diameter (mm)	190+	190+	140	190+	150	
	50 mm	*Flow Rate (L/sec)*	1.45	1.33	1.31	1.36	1.46	1.382
		Height (mm)	250+	250+	250+	250+	0	
		Diameter (mm)	190+	170	110	180	0	
	80 mm	*Flow Rate (L/sec)*	1.42	1.48	1.28	1.53	1.49	1.44
		Height (mm)	250+	250+	250+	250+	0	
		Diameter (mm)	190+	170	90	180	0	

Well 4

			Limestone			Mussel Shells		
			AgLime	2.36-5mm	5-10 mm	4-12mm	Whole/broken	Mean Flow Rate
	Inlet Pipe Diameter							
Well 4 (White 10 L bucket)	15 mm	*Flow rate L/sec*	0.81	0.79	0.63	0.88	0.89	0.8
		Height (mm)	270+	80	0	0	0	
		Diameter (mm)	250	70	0	0	0	
	20 mm	*Flow Rate (L/sec)*	1.47	1.14	1.04	1.29	1.25	1.238
		Height (mm)	270+	80	100	100	0	
		Diameter (mm)	260+	110	30	85	0	
	25 mm	*Flow Rate (L/sec)*	1.1	1.32	1.16	1.48	1.49	1.31
		Height (mm)	270+	110	170	270+	0	
		Diameter (mm)	260+	50	100	130	0	
	32 mm	*Flow Rate (L/sec)*	1.03	1.44	x	1.49	1.45	1.3525
		Height (mm)	270+	270+	270+	270+	70	
		Diameter (mm)	250	90	160	190	35	
	40 mm	*Flow Rate (L/sec)*	1.04	1.43	1.36	1.46	1.52	1.362
		Height (mm)	270+	270+	180	270+	270+	
		Diameter (mm)	240	210	160	170	50	
	50 mm	*Flow Rate (L/sec)*	1	1.34	1.35	1.38	1.43	1.3
		Height (mm)	270+	270+	90	270+	0	
		Diameter (mm)	150	250	70	130	0	
	80 mm	*Flow Rate (L/sec)*	1.12	1.46	1.32	1.42	1.47	1.358
		Height (mm)	270+	270+	100	270+	0	
		Diameter (mm)	100	240	90	110	0	

Appendix C

Figure 6.4 *Left; mulcher used to crush mussel shell substrate. Right; sieve used to sieve mussel shell grains to <4.5 mm.*

Figure 6.5 *Left; YSI equipment used to measure pH level, electric conductivity and dissolved oxygen levels. Right; sample bottles used to sample sulphates, total and dissolved metal concentrations (these samples were then sent to Hills Lab following each site visit).*

Appendix D

Samples were sent to Hills Laboratories for chemical analysis (total, dissolved and sulphate concentrations). The following are the reports.

Hill Laboratories
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R J Hill Laboratories Limited
1 Clyde Street Hamilton 3216
Private Bag 3205
Hamilton 3240 New Zealand

T 0508 HILL LAB (44 555 22)
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

ANALYSIS REPORT

Client:	CRL Energy Limited	Lab No:	1812235	SPv1
Contact:	Emma Forbes	Date Received:	20-Jul-2017	
	C/- CRL Energy Limited	Date Reported:	01-Aug-2017	
	PO Box 29415	Quote No:		
	Christchurch 8540	Order No:		
		Client Reference:		
		Submitted By:	Emma Forbes	

Sample Type: Aqueous

Sample Name:		Inlet AMD 19-Jul-2017 3:30 pm	Outlet Initial Mussel Shells 19-Jul-2017 3:45 pm	Outlet 15min Mussel Shells 19-Jul-2017 4:00 pm	Outlet 30min Mussel Shells 19-Jul-2017 4:15 pm	Outlet Initial Limestone 20-Jul-2017 9:00 am
Lab Number:		1812235.1	1812235.2	1812235.3	1812235.4	1812235.5
Dissolved Aluminium	g/m³	40 #1	35 #1	35 #1	36 #1	0.168
Total Aluminium	g/m³	39 #1	34 #1	34 #1	34 #1	14.1
Dissolved Iron	g/m³	83	61	61	60	22
Total Iron	g/m³	84	62	61	62	43
Dissolved Manganese	g/m³	0.82 #1	0.75 #1	0.76 #1	0.77 #1	0.81 #1
Total Manganese	g/m³	0.72 #1	0.68 #1	0.67 #1	0.68 #1	0.78 #1
Dissolved Nickel	g/m³	0.137 #1	0.121	0.126 #1	0.127	0.122 #1
Total Nickel	g/m³	0.130 #1	0.123	0.120 #1	0.121	0.121 #1
Dissolved Zinc	g/m³	0.34 #1	0.28 #1	0.28	0.27	0.198
Total Zinc	g/m³	0.33 #1	0.27 #1	0.28	0.27	0.23
Sulphate	g/m³	740	690	700	690	1,970

Sample Name:		Outlet 15min Limestone 20-Jul-2017 9:15 am	Outlet 30min Limestone 20-Jul-2017 9:30 am			
Lab Number:		1812235.6	1812235.7			
Dissolved Aluminium	g/m³	32	33	-	-	-
Total Aluminium	g/m³	32	33	-	-	-
Dissolved Iron	g/m³	53	55	-	-	-
Total Iron	g/m³	56	56	-	-	-
Dissolved Manganese	g/m³	0.76 #1	0.76 #1	-	-	-
Total Manganese	g/m³	0.69 #1	0.69 #1	-	-	-
Dissolved Nickel	g/m³	0.121 #1	0.125 #1	-	-	-
Total Nickel	g/m³	0.119 #1	0.121 #1	-	-	-
Dissolved Zinc	g/m³	0.27	0.27	-	-	-
Total Zinc	g/m³	0.27	0.27	-	-	-
Sulphate	g/m³	700	710	-	-	-

Analyst's Comments

#1 It has been noted that the result for the dissolved fraction was greater than that for the total fraction, but within analytical variation of the methods.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter.	-	1-7

Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-7
Dissolved Aluminium	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.003 g/m³	1-7
Total Aluminium	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0032 g/m³	1-7
Dissolved Iron	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.02 g/m³	1-7
Total Iron	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.021 g/m³	1-7
Dissolved Manganese	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-7
Total Manganese	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-7
Dissolved Nickel	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-7
Total Nickel	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-7
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m³	1-7
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m³	1-7
Sulphate	Filtered sample. Ion Chromatography. APHA 4110 B 22nd ed. 2012.	0.5 g/m³	1-7

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Carole Rodgers-Carroll BA, NZCS
Client Services Manager - Environmental

Hill Laboratories
TRIED, TESTED AND TRUSTED
R J Hill Laboratories Limited
28 Duke Street Frankton 3204
Private Bag 3205
Hamilton 3240 New Zealand
T 0508 HILL LAB (44 555 22)
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

ANALYSIS REPORT

Client:	CRL Energy Limited	Lab No:	1846515	SPv1
Contact:	Emma Forbes	Date Received:	20-Sep-2017	
	C/- CRL Energy Limited	Date Reported:	28-Sep-2017	
	PO Box 29415	Quote No:		
	Christchurch 8540	Order No:		
		Client Reference:	Limestone Trials	
		Submitted By:	Emma Forbes	

Sample Type: Aqueous

Sample Name:		DW Bucket 1 - Initial 14-Sep-2017	DW Bucket 2 - Initial 14-Sep-2017	DW Bucket 3 - Initial 14-Sep-2017	DW Bucket 1- 30 Minutes 14-Sep-2017	DW Bucket 2- 30 Minutes 14-Sep-2017
Lab Number:		1846515.1	1846515.2	1846515.3	1846515.4	1846515.5
Dissolved Aluminium	g/m³	0.056	0.051	0.047	0.041	0.043
Total Aluminium	g/m³	5.3	3.9	1.92	2.5	2.3
Dissolved Iron	g/m³	1.63	1.44	1.42	1.51	1.42
Total Iron	g/m³	9.8	7.8	4.7	5.7	5.2
Dissolved Manganese	g/m³	0.56	0.55	0.55	0.56	0.56
Total Manganese	g/m³	0.58	0.58	0.55	0.57	0.56
Dissolved Nickel	g/m³	0.088	0.083	0.082	0.088	0.083
Total Nickel	g/m³	0.104	0.098	0.091	0.096	0.091
Dissolved Zinc	g/m³	0.064	0.057	0.054	0.060	0.057
Total Zinc	g/m³	0.098	0.096	0.072	0.080	0.075
Sulphate	g/m³	480	470	480	450	430

Sample Name:		DW Bucket 3 - 30 Minutes 14-Sep-2017	DW Bucket 1 - 18 Hour 15-Sep-2017	DW Bucket 2 - 18 Hour 15-Sep-2017	DW Bucket 3 - 18 Hour 15-Sep-2017	DW Bucket 4 - 1 Hour 14-Sep-2017
Lab Number:		1846515.6	1846515.7	1846515.8	1846515.9	1846515.10
Dissolved Aluminium	g/m³	0.046	0.026	0.016	0.015	29
Total Aluminium	g/m³	1.90	0.32	0.26	0.44	29
Dissolved Iron	g/m³	1.38	1.17	0.98	0.86	31
Total Iron	g/m³	4.7	1.94	1.68	1.75	33
Dissolved Manganese	g/m³	0.56	0.56	0.56	0.56	0.62
Total Manganese	g/m³	0.56	0.56	0.56	0.56	0.62
Dissolved Nickel	g/m³	0.081	0.086	0.082	0.079	0.102
Total Nickel	g/m³	0.090	0.090	0.083	0.082	0.106
Dissolved Zinc	g/m³	0.055	0.059	0.054	0.053	0.25
Total Zinc	g/m³	0.071	0.068	0.061	0.062	0.27
Sulphate	g/m³	450	490	460	490	610

Sample Name:		Inlet AMD 14-Sep-2017	Settling Pond - Initial 14-Sep-2017	Settling Pond - 30 Minutes 14-Sep-2017	Settling Pond - 1 Hour 14-Sep-2017	Settling Pond - 18 Hours 15-Sep-2017
Lab Number:		1846515.11	1846515.12	1846515.13	1846515.14	1846515.15
Dissolved Aluminium	g/m³	31 #1	0.065	28	29 #1	30 #1
Total Aluminium	g/m³	29 #1	10.3	28	28 #1	28 #1
Dissolved Iron	g/m³	34	3.4	23	27	37
Total Iron	g/m³	34	16.4	32	33	38
Dissolved Manganese	g/m³	0.62 #1	0.64	0.62	0.62	0.61
Total Manganese	g/m³	0.61 #1	0.65	0.62	0.62	0.61
Dissolved Nickel	g/m³	0.104	0.097	0.102	0.101	0.100
Total Nickel	g/m³	0.105	0.111	0.107	0.106	0.102
Dissolved Zinc	g/m³	0.26	0.163	0.25	0.25	0.25

IANZ ACCREDITED LABORATORY

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The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Sample Type: Aqueous						
Sample Name:		Inlet AMD 14-Sep-2017	Settling Pond - Initial 14-Sep-2017	Settling Pond - 30 Minutes 14-Sep-2017	Settling Pond - 1 Hour 14-Sep-2017	Settling Pond - 18 Hours 15-Sep-2017
Lab Number:		1846515.11	1846515.12	1846515.13	1846515.14	1846515.15
Total Zinc	g/m³	0.27	0.21	0.26	0.27	0.27
Sulphate	g/m³	610	600	600	590	590

Analyst's Comments

#1 It has been noted that the result for the dissolved fraction was greater than that for the total fraction, but within analytical variation of the methods.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter. Performed at Hill Laboratories - Chemistry, 101c Waterloo Road, Christchurch.	-	1-15
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-15
Dissolved Aluminium	Filtered sample, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012.	0.003 g/m³	1-15
Total Aluminium	Nitric acid digestion, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0032 g/m³	1-15
Dissolved Iron	Filtered sample, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012.	0.02 g/m³	1-15
Total Iron	Nitric acid digestion, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012.	0.021 g/m³	1-15
Dissolved Manganese	Filtered sample, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-15
Total Manganese	Nitric acid digestion, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-15
Dissolved Nickel	Filtered sample, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-15
Total Nickel	Nitric acid digestion, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-15
Dissolved Zinc	Filtered sample, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012.	0.0010 g/m³	1-15
Total Zinc	Nitric acid digestion, ICP-MS, trace level. Analysed at 1 Clyde Street, Hamilton. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m³	1-15
Sulphate	Filtered sample from Christchurch. Ion Chromatography. APHA 4110 B 22nd ed. 2012.	0.5 g/m³	1-15

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Ara Heron BSc (Tech)
Client Services Manager - Environmental

Hill Laboratories
TRIED, TESTED AND TRUSTED

R J Hill Laboratories Limited
28 Duke Street Frankton 3204
Private Bag 3205
Hamilton 3240 New Zealand

T 0508 HILL LAB (44 555 22)
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

ANALYSIS REPORT

Client:	CRL Energy Limited	Lab No:	1864786	SPv1
Contact:	Emma Forbes	Date Received:	24-Oct-2017	
	C/- CRL Energy Limited	Date Reported:	06-Nov-2017	
	PO Box 29415	Quote No:		
	Christchurch 8540	Order No:		
		Client Reference:		
		Submitted By:	Emma Forbes	

Sample Type: Aqueous

Sample Name:		Limestone Inlet AMD 22-Oct-2017	Limestone Settling Pond Initial 22-Oct-2017	Limestone Settling Pond 30 min 22-Oct-2017	Limestone Settling Pond 1 hour 22-Oct-2017	Limestone Settling Pond 18+ hours 23-Oct-2017
Lab Number:		1864786.1	1864786.2	1864786.3	1864786.4	1864786.5
Dissolved Aluminium	g/m³	27 #1	0.139	25	29 #1	32 #1
Total Aluminium	g/m³	24 #1	21	25	26 #1	29 #1
Dissolved Iron	g/m³	33 #1	19.5	22	32	38 #1
Total Iron	g/m³	32 #1	33	33	33	37 #1
Dissolved Manganese	g/m³	0.53	0.62	0.58	0.56	0.62
Total Manganese	g/m³	0.56	0.72	0.62	0.63	0.65
Dissolved Nickel	g/m³	0.087	0.095	0.099	0.097	0.110
Total Nickel	g/m³	0.092	0.111	0.103	0.099	0.110
Dissolved Zinc	g/m³	0.21	0.177	0.22	0.24	0.26
Total Zinc	g/m³	0.22	0.23	0.24	0.26	0.30
Sulphate	g/m³	590	570	580	580	610

Sample Name:		Limestone Bucket 1 Initial 22-Oct-2017	Limestone Bucket 2 Initial 22-Oct-2017	Limestone Bucket 3 Initial 22-Oct-2017	Limestone Bucket 4 Initial 22-Oct-2017	Limestone Bucket 1 18+ hours 23-Oct-2017
Lab Number:		1864786.6	1864786.7	1864786.8	1864786.9	1864786.10
Dissolved Aluminium	g/m³	0.054	29 #1	29 #1	28 #1	0.017
Total Aluminium	g/m³	19.9	25 #1	26 #1	27 #1	3.0
Dissolved Iron	g/m³	18.2	32	33	32	11.4
Total Iron	g/m³	45	32	33	33	19.2
Dissolved Manganese	g/m³	0.63	0.56	0.58	0.57	0.67
Total Manganese	g/m³	1.12	0.61	0.63	0.61	0.71
Dissolved Nickel	g/m³	0.090	0.099	0.095	0.094	0.085
Total Nickel	g/m³	0.133	0.104	0.102	0.099	0.095
Dissolved Zinc	g/m³	0.102	0.23	0.22	0.23	0.072
Total Zinc	g/m³	0.199	0.23	0.24	0.23	0.097
Sulphate	g/m³	540	590	580	570	550

Sample Name:		Limestone Bucket 2 18+ hours 23-Oct-2017	Limestone Bucket 3 18+ hours 23-Oct-2017	Limestone Bucket 4 18+ hours 23-Oct-2017		
Lab Number:		1864786.11	1864786.12	1864786.13		
Dissolved Aluminium	g/m³	30 #1	30 #1	30 #1	-	-
Total Aluminium	g/m³	25 #1	24 #1	25 #1	-	-
Dissolved Iron	g/m³	23	23	26	-	-
Total Iron	g/m³	25	25	28	-	-
Dissolved Manganese	g/m³	0.60	0.59	0.57	-	-
Total Manganese	g/m³	0.63	0.61	0.62	-	-
Dissolved Nickel	g/m³	0.094	0.095	0.101	-	-
Total Nickel	g/m³	0.102	0.098	0.101	-	-

IANZ ACCREDITED LABORATORY

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The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Sample Type: Aqueous						
Sample Name:		Limestone Bucket 2 18+ hours 23-Oct-2017	Limestone Bucket 3 18+ hours 23-Oct-2017	Limestone Bucket 4 18+ hours 23-Oct-2017		
Lab Number:		1864786.11	1864786.12	1864786.13		
Dissolved Zinc	g/m³	0.24	0.23	0.28	-	-
Total Zinc	g/m³	0.24	0.24	0.29	-	-
Sulphate	g/m³	580	580	580	-	-

Analyst's Comments

#1 It has been noted that the result for the dissolved fraction was greater than that for the total fraction, but within analytical variation of the methods.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter. Performed at Hill Laboratories - Chemistry, 101c Waterloo Road, Christchurch.	-	1-13
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-13
Dissolved Aluminium	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.003 g/m³	1-13
Total Aluminium	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0032 g/m³	1-13
Dissolved Iron	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.02 g/m³	1-13
Total Iron	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.021 g/m³	1-13
Dissolved Manganese	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-13
Total Manganese	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-13
Dissolved Nickel	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-13
Total Nickel	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-13
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m³	1-13
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m³	1-13
Sulphate	Filtered sample from Christchurch. Ion Chromatography. APHA 4110 B 22nd ed. 2012.	0.5 g/m³	1-13

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Carole Rodgers-Carroll BA, NZCS
Client Services Manager - Environmental

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R J Hill Laboratories Limited
28 Duke Street Frankton 3204
Private Bag 3205
Hamilton 3240 New Zealand

T 0508 HILL LAB (44 555 22)
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

ANALYSIS REPORT

Client:	CRL Energy Limited	Lab No:	1904669 SPv1
Contact:	Emma Forbes	Date Received:	09-Jan-2018
	C/- CRL Energy Limited	Date Reported:	16-Jan-2018
	PO Box 29415	Quote No:	
	Christchurch 8540	Order No:	
		Client Reference:	
		Submitted By:	Emma Forbes

Sample Type: Aqueous

Sample Name:		Limestone Inlet AMD 22-Dec-2017	Limestone Initial 22-Dec-2017	Limestone 15 Min 22-Dec-2017	Limestone 30 Min 22-Dec-2017	Limestone 1 Hour 22-Dec-2017
Lab Number:		1904669.1	1904669.2	1904669.3	1904669.4	1904669.5
pH	pH Units	2.8	6.2	5.3	3.2	2.9
Dissolved Aluminium	g/m³	54 #1	1.81	15.3	39	50 #1
Total Aluminium	g/m³	49 #1	37	39	46	48 #1
Dissolved Iron	g/m³	121 #1	115	110	114	125 #1
Total Iron	g/m³	108 #1	118	118	116	119 #1
Dissolved Manganese	g/m³	0.96 #1	1.06 #1	1.02 #1	0.97 #1	0.94 #1
Total Manganese	g/m³	0.91 #1	1.02 #1	0.96 #1	0.93 #1	0.92 #1
Dissolved Nickel	g/m³	0.165 #1	0.158	0.159 #1	0.156 #1	0.158 #1
Total Nickel	g/m³	0.151 #1	0.158	0.155 #1	0.149 #1	0.152 #1
Dissolved Zinc	g/m³	0.45 #1	0.40	0.40 #1	0.41 #1	0.42 #1
Total Zinc	g/m³	0.42 #1	0.40	0.39 #1	0.40 #1	0.40 #1
Sulphate	g/m³	990	890	900	850	920

Analyst's Comments

#1 It has been noted that the result for the dissolved fraction was greater than that for the total fraction, but within analytical variation of the methods.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter. Performed at Hill Laboratories - Chemistry, 101c Waterloo Road, Christchurch.	-	1-5
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-5
pH	pH meter. Analysed at Hill Laboratories - Chemistry, 101c Waterloo Road, Christchurch. APHA 4500-H+ B 22nd ed. 2012. Note: It is not possible to achieve the APHA Maximum Storage Recommendation for this test (15 min) when samples are analysed upon receipt at the laboratory, and not in the field.	0.1 pH Units	1-5
Dissolved Aluminium	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.003 g/m³	1-5
Total Aluminium	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0032 g/m³	1-5
Dissolved Iron	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.02 g/m³	1-5
Total Iron	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.021 g/m³	1-5
Dissolved Manganese	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-5

Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Total Manganese	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-5
Dissolved Nickel	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-5
Total Nickel	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-5
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m³	1-5
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m³	1-5
Sulphate	Filtered sample from Christchurch. Ion Chromatography. APHA 4110 B 22nd ed. 2012.	0.5 g/m³	1-5

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Ara Heron BSc (Tech)
Client Services Manager - Environmental

Hill Laboratories
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R J Hill Laboratories Limited
28 Duke Street Frankton 3204
Private Bag 3205
Hamilton 3240 New Zealand

T 0508 HILL LAB (44 555 22)
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

ANALYSIS REPORT

Client:	CRL Energy Limited	Lab No:	1864785	SPv1
Contact:	Emma Forbes	Date Received:	24-Oct-2017	
	C/- CRL Energy Limited	Date Reported:	06-Nov-2017	
	PO Box 29415	Quote No:		
	Christchurch 8540	Order No:		
		Client Reference:		
		Submitted By:	Emma Forbes	

Sample Type: Aqueous

Sample Name:		Mussel Shells Inlet AMD 21-Oct-2017	Shells Settling Pond Initial 21-Oct-2017	Shells Settling Pond 30min 21-Oct-2017	Shells Settling Pond 1 Hour 21-Oct-2017	Shells Settling Pond 18+ Hours 21-Oct-2017
Lab Number:		1864785.1	1864785.2	1864785.3	1864785.4	1864785.5
Dissolved Aluminium	g/m³	32 #1	21	29	32	30
Total Aluminium	g/m³	31 #1	25	31	32	32
Dissolved Iron	g/m³	31	5.2	25	29	33
Total Iron	g/m³	32	26	30	30	34
Dissolved Manganese	g/m³	0.60	0.60	0.60	0.60	0.56
Total Manganese	g/m³	0.61	0.66	0.61	0.62	0.59
Dissolved Nickel	g/m³	0.105	0.095	0.102	0.103	0.100
Total Nickel	g/m³	0.111	0.105	0.111	0.108	0.102
Dissolved Zinc	g/m³	0.26 #1	0.22	0.25 #1	0.24	0.24
Total Zinc	g/m³	0.24 #1	0.22	0.23 #1	0.24	0.24
Sulphate	g/m³	600	620	620	620	610

Sample Name:		Shells Bucket 1 Initial 21-Oct-2017	Shells Bucket 2 Initial 21-Oct-2017	Shells Bucket 3 Initial 21-Oct-2017	Shells Bucket 4 Initial 21-Oct-2017	Shells Bucket 1 18+ Hours 22-Oct-2017
Lab Number:		1864785.6	1864785.7	1864785.8	1864785.9	1864785.10
Dissolved Aluminium	g/m³	0.011	29	31	30	0.015
Total Aluminium	g/m³	1.06	30	32	32	0.59
Dissolved Iron	g/m³	0.12	25	29	29	2.3
Total Iron	g/m³	8.3	30	32	30	5.5
Dissolved Manganese	g/m³	0.57	0.60	0.60	0.60	0.56
Total Manganese	g/m³	0.59	0.64	0.63	0.63	0.59
Dissolved Nickel	g/m³	0.044	0.101	0.106	0.103	0.048
Total Nickel	g/m³	0.059	0.109	0.110	0.110	0.052
Dissolved Zinc	g/m³	0.031	0.26	0.25	0.25 #1	0.034
Total Zinc	g/m³	0.068	0.26	0.25	0.24 #1	0.053
Sulphate	g/m³	570	620	620	620	590

Sample Name:		Shells Bucket 2 18+ Hours 22-Oct-2017	Shells Bucket 3 18+ Hours 22-Oct-2017	Shells Bucket 4 18+ Hours 22-Oct-2017		
Lab Number:		1864785.11	1864785.12	1864785.13		
Dissolved Aluminium	g/m³	24	30	31 #1	-	-
Total Aluminium	g/m³	28	31	29 #1	-	-
Dissolved Iron	g/m³	7.0	18.4	27	-	-
Total Iron	g/m³	18.6	24	29	-	-
Dissolved Manganese	g/m³	0.59	0.59	0.61	-	-
Total Manganese	g/m³	0.61	0.61	0.62	-	-
Dissolved Nickel	g/m³	0.100	0.101	0.102	-	-
Total Nickel	g/m³	0.107	0.107	0.109	-	-
Dissolved Zinc	g/m³	0.27	0.25	0.25	-	-

Sample Type: Aqueous						
Sample Name:		Shells Bucket 2 18+ Hours 22-Oct-2017	Shells Bucket 3 18+ Hours 22-Oct-2017	Shells Bucket 4 18+ Hours 22-Oct-2017		
Lab Number:		1864785.11	1864785.12	1864785.13		
Total Zinc	g/m³	0.27	0.25	0.26	-	-
Sulphate	g/m³	610	610	620	-	-

Analyst's Comments

#1 It has been noted that the result for the dissolved fraction was greater than that for the total fraction, but within analytical variation of the methods.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter. Performed at Hill Laboratories - Chemistry, 101c Waterloo Road, Christchurch.	-	1-13
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-13
Filtration for dissolved metals analysis	Sample filtration through 0.45µm membrane filter and preservation with nitric acid. APHA 3030 B 22nd ed. 2012.	-	6
Dissolved Aluminium	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.003 g/m³	1-13
Total Aluminium	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0032 g/m³	1-13
Dissolved Iron	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.02 g/m³	1-13
Total Iron	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.021 g/m³	1-13
Dissolved Manganese	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-13
Total Manganese	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-13
Dissolved Nickel	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-13
Total Nickel	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-13
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m³	1-13
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m³	1-13
Sulphate	Filtered sample from Christchurch. Ion Chromatography. APHA 4110 B 22nd ed. 2012.	0.5 g/m³	1-13

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W www.hill-laboratories.com

ANALYSIS REPORT

Client:	CRL Energy Limited	Lab No:	1904668	SPv1
Contact:	Emma Forbes	Date Received:	09-Jan-2018	
	C/- CRL Energy Limited	Date Reported:	16-Jan-2018	
	PO Box 29415	Quote No:		
	Christchurch 8540	Order No:		
		Client Reference:		
		Submitted By:	Emma Forbes	

Sample Type: Aqueous

Sample Name:	Mussel Shells Inlet AMD 22-Dec-2017	Mussel Shells Initial 22-Dec-2017	Mussel Shells 15 Min 22-Dec-2017	Mussel Shells 30 Min 22-Dec-2017	Mussel Shells 1 Hour 22-Dec-2017
Lab Number:	1904668.1	1904668.2	1904668.3	1904668.4	1904668.5
pH pH Units	2.8	3.5	3.0	2.9	2.9
Dissolved Aluminium g/m³	47	32	40	43	44
Total Aluminium g/m³	50	38	42	44	46
Dissolved Iron g/m³	115 #1	90	100	113	119 #1
Total Iron g/m³	114 #1	106	111	114	116 #1
Dissolved Manganese g/m³	0.93 #1	0.90 #1	0.93 #1	0.92 #1	0.89 #1
Total Manganese g/m³	0.92 #1	0.86 #1	0.87 #1	0.87 #1	0.86 #1
Dissolved Nickel g/m³	0.154 #1	0.145 #1	0.151 #1	0.150 #1	0.155 #1
Total Nickel g/m³	0.151 #1	0.141 #1	0.143 #1	0.147 #1	0.141 #1
Dissolved Zinc g/m³	0.42	0.38	0.39	0.40 #1	0.40 #1
Total Zinc g/m³	0.44	0.39	0.40	0.39 #1	0.39 #1
Sulphate g/m³	960	860	830	910	940

Sample Name:	Mussel Shells 18+ Hours 22-Dec-2017				
Lab Number:	1904668.6				
pH pH Units	2.9	-	-	-	-
Dissolved Aluminium g/m³	55 #1	-	-	-	-
Total Aluminium g/m³	49 #1	-	-	-	-
Dissolved Iron g/m³	131 #1	-	-	-	-
Total Iron g/m³	122 #1	-	-	-	-
Dissolved Manganese g/m³	0.93 #1	-	-	-	-
Total Manganese g/m³	0.87 #1	-	-	-	-
Dissolved Nickel g/m³	0.154 #1	-	-	-	-
Total Nickel g/m³	0.148 #1	-	-	-	-
Dissolved Zinc g/m³	0.44 #1	-	-	-	-
Total Zinc g/m³	0.42 #1	-	-	-	-
Sulphate g/m³	1,000	-	-	-	-

Analyst's Comments

#1 It has been noted that the result for the dissolved fraction was greater than that for the total fraction, but within analytical variation of the methods.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No

IANZ ACCREDITED LABORATORY

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The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter. Performed at Hill Laboratories - Chemistry; 101c Waterloo Road, Christchurch.	-	1-6
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-6
pH	pH meter. Analysed at Hill Laboratories - Chemistry; 101c Waterloo Road, Christchurch. APHA 4500-H^+ B 22nd ed. 2012. Note: It is not possible to achieve the APHA Maximum Storage Recommendation for this test (15 min) when samples are analysed upon receipt at the laboratory, and not in the field.	0.1 pH Units	1-6
Dissolved Aluminium	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.003 g/m³	1-6
Total Aluminium	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0032 g/m³	1-6
Dissolved Iron	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.02 g/m³	1-6
Total Iron	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.021 g/m³	1-6
Dissolved Manganese	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-6
Total Manganese	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-6
Dissolved Nickel	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-6
Total Nickel	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-6
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m³	1-6
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m³	1-6
Sulphate	Filtered sample from Christchurch. Ion Chromatography. APHA 4110 B 22nd ed. 2012.	0.5 g/m³	1-6

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Client Services Manager - Environmental

Hill Laboratories
TRIED, TESTED AND TRUSTED
R J Hill Laboratories Limited
28 Duke Street Frankton 3204
Private Bag 3205
Hamilton 3240 New Zealand
T 0508 HILL LAB (44 555 22)
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

ANALYSIS REPORT

Client:	CRL Energy Limited	Lab No:	1914684 SPv1
Contact:	Emma Forbes	Date Received:	26-Jan-2018
	C/- CRL Energy Limited	Date Reported:	07-Feb-2018
	PO Box 29415	Quote No:	
	Christchurch 8540	Order No:	
		Client Reference:	
		Submitted By:	Emma Forbes

Sample Type: Aqueous

Sample Name:		Mussel Shells Inlet AMD 23-Jan-2018	Mussel Shells Initial 23-Jan-2018	Mussel Shells 15 Min 23-Jan-2018	Mussel Shells 30 Min 23-Jan-2018	Mussel Shells 1 Hour 23-Jan-2018
Lab Number:		1914684.1	1914684.2	1914684.3	1914684.4	1914684.5
Dissolved Aluminium	g/m³	28	26	33 #1	33 #1	33 #1
Total Aluminium	g/m³	30	28	30 #1	31 #1	31 #1
Dissolved Iron	g/m³	29	28	51	55	55
Total Iron	g/m³	29	49	55	55	58
Dissolved Manganese	g/m³	0.52	0.70	0.71	0.71	0.70
Total Manganese	g/m³	0.54	0.75	0.74	0.73	0.74
Dissolved Nickel	g/m³	0.101 #1	0.123 #1	0.121 #1	0.122	0.120 #1
Total Nickel	g/m³	0.098 #1	0.118 #1	0.119 #1	0.122	0.118 #1
Dissolved Zinc	g/m³	0.28	0.28 #1	0.29 #1	0.29 #1	0.29 #1
Total Zinc	g/m³	0.29	0.27 #1	0.28 #1	0.28 #1	0.28 #1
Sulphate	g/m³	530	760	730	720	710

Sample Name:		Mussel Shells 18+ Hours 23-Jan-2018				
Lab Number:		1914684.6				
Dissolved Aluminium	g/m³	34 #1	-	-	-	-
Total Aluminium	g/m³	30 #1	-	-	-	-
Dissolved Iron	g/m³	57 #1	-	-	-	-
Total Iron	g/m³	55 #1	-	-	-	-
Dissolved Manganese	g/m³	0.68	-	-	-	-
Total Manganese	g/m³	0.72	-	-	-	-
Dissolved Nickel	g/m³	0.128 #1	-	-	-	-
Total Nickel	g/m³	0.122 #1	-	-	-	-
Dissolved Zinc	g/m³	0.29 #1	-	-	-	-
Total Zinc	g/m³	0.28 #1	-	-	-	-
Sulphate	g/m³	700	-	-	-	-

Analyst's Comments

#1 It has been noted that the result for the dissolved fraction was greater than that for the total fraction, but within analytical variation of the methods.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter. Performed at Hill Laboratories - Chemistry; 101c Waterloo Road, Christchurch.	-	1-6
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-6

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Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Dissolved Aluminium	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.003 g/m³	1-6
Total Aluminium	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0032 g/m³	1-6
Dissolved Iron	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.02 g/m³	1-6
Total Iron	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.021 g/m³	1-6
Dissolved Manganese	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-6
Total Manganese	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-6
Dissolved Nickel	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-6
Total Nickel	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-6
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m³	1-6
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m³	1-6
Sulphate	Filtered sample from Christchurch. Ion Chromatography. APHA 4110 B 22nd ed. 2012.	0.5 g/m³	1-6

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Carole Rodgers-Carroll BA, NZCS
Client Services Manager - Environmental

Hill Laboratories
TRIED, TESTED AND TRUSTED

R J Hill Laboratories Limited
28 Duke Street Frankton 3204
Private Bag 3205
Hamilton 3240 New Zealand

T 0508 HILL LAB (44 555 22)
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

ANALYSIS REPORT

Client:	CRL Energy Limited	Lab No:	1914685 SPv1
Contact:	Emma Forbes	Date Received:	26-Jan-2018
	C/- CRL Energy Limited	Date Reported:	05-Feb-2018
	PO Box 29415	Quote No:	
	Christchurch 8540	Order No:	
		Client Reference:	
		Submitted By:	Emma Forbes

Sample Type: Aqueous

Sample Name:		Mixed Inlet AMD 24-Jan-2018	Mised Initial 24-Jan-2018	Mixed 15 Min 24-Jan-2018	Mixed 30 Min 24-Jan-2018	Mixed 1 Hour 24-Jan-2018
Lab Number:		1914685.1	1914685.2	1914685.3	1914685.4	1914685.5
Dissolved Aluminium	g/m³	38 #1	13.8	30 #1	33 #1	33 #1
Total Aluminium	g/m³	34 #1	24	29 #1	30 #1	31 #1
Dissolved Iron	g/m³	59	39	46	54	55
Total Iron	g/m³	61	55	54	56	56
Dissolved Manganese	g/m³	0.75	0.75	0.71	0.71	0.69
Total Manganese	g/m³	0.76	0.79	0.74	0.71	0.72
Dissolved Nickel	g/m³	0.124	0.110	0.113	0.112	0.110
Total Nickel	g/m³	0.129	0.118	0.116	0.114	0.117
Dissolved Zinc	g/m³	0.30	0.25	0.26	0.27	0.27
Total Zinc	g/m³	0.30	0.26	0.27	0.27	0.27
Sulphate	g/m³	760	710	710	700	710

Analyst's Comments

#1 It has been noted that the result for the dissolved fraction was greater than that for the total fraction, but within analytical variation of the methods.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter. Performed at Hill Laboratories - Chemistry; 101c Waterloo Road, Christchurch.	-	1-5
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-5
Dissolved Aluminium	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.003 g/m³	1-5
Total Aluminium	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0032 g/m³	1-5
Dissolved Iron	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.02 g/m³	1-5
Total Iron	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.021 g/m³	1-5
Dissolved Manganese	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-5
Total Manganese	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-5
Dissolved Nickel	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m³	1-5
Total Nickel	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m³	1-5
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m³	1-5

IANZ ACCREDITED LABORATORY

This Laboratory is accredited by International Accreditation New Zealand (IANZ), which represents New Zealand in the International Laboratory Accreditation Cooperation (ILAC). Through the ILAC Mutual Recognition Arrangement (ILAC-MRA) this accreditation is internationally recognised.
The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m³	1-5
Sulphate	Filtered sample from Christchurch. Ion Chromatography. APHA 4110 B 22nd ed. 2012.	0.5 g/m³	1-5

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Ara Heron BSc (Tech)
Client Services Manager - Environmental

Appendix E

Raw data results of diversion well set-up at Bellvue Mine. Water samples for total and dissolved metal concentrations and water quality parameters (sulphate, pH level, dissolved oxygen and electric conductivity) were collected. Inlet acidic mine water were sampled at the beginning of each test, followed by samples of treated waters over several hours. The data set consists of four limestone and three mussel shell treatment tests and one mixed substrate test. These results were averaged and are discussed in Chapter 3.

x Indicates no data collected. Equipment error, invalid results or sample not tested

* Not included in averaged results (outlier)

Note some dissolved metal concentrations are greater than the equivalent total metal concentration but within analytical variation of the methods.

Limestone 1 Data Set

Limestone 1 19/07/2017			Inlet AMD	Settling Pond Initial	Settling Pond 15 minutes	Settling Pond 30 minutes	Settling Pond 1 hour	Settling Pond 18 hours
Water Chemistry	Total (g/m3)	Al	39	14.1	32	33	x	x
		Fe	84	43	56	56	x	x
		Mn	0.72	0.78	0.69	0.69	x	x
		Ni	0.13	0.121	0.119	0.121	x	x
		Zn	0.33	0.23	0.27	0.27	x	x
	Dissolved (g/m3)	Al	40	0.168	32	33	x	x
		Fe	83	22	53	55	x	x
		Mn	0.82	0.81	0.76	0.76	x	x
		Ni	0.137	0.122	0.121	0.125	x	x
		Zn	0.34	0.198	0.27	0.27	x	x
		Sulphate (g/m3)	740	1970	700	710	x	x
Water Quality Parameter		pH	2.71	5.81	3.04	2.89	x	x
		DO (%)	37.4	68.2	55.1	52.7	x	x
		EC (µs/cm)	1100	976	1047	1122	x	x

Limestone 2 Data Set

Limestone 2 14/09/2017			Inlet AMD	Settling Pond Initial	Settling Pond 15 minutes	Settling Pond 30 minutes	Settling Pond 1 hour	Settling Pond 18 hours
Water Chemistry	Total (g/m3)	Al	29	10.3	x	28	28	28
		Fe	34	16.4	x	32	33	38
		Mn	0.61	0.65	x	0.62	0.62	0.61
		Ni	0.105	0.111	x	0.107	0.106	0.102
		Zn	0.27	0.21	x	0.26	0.27	0.27
	Dissolved (g/m3)	Al	31	0.065	x	28	29	30
		Fe	34	3.4	x	23	27	37
		Mn	0.62	0.64	x	0.62	0.62	0.61
		Ni	0.104	0.097	x	0.102	0.101	0.1
		Zn	0.26	0.163	x	0.25	0.25	0.25
		Sulphate (g/m3)	610	600	x	600	590	590
Water Quality Parameters		pH	2.7	5.96	x	3.46	3.33	2.98
		DO (%)	37.7	54.5	x	51.8	51.4	63.4
		EC (µs/cm)	1358	942	x	873	894	1055

Limestone 3 Data Set

Limestone 3 21/10/2017			Inlet AMD	Settling Pond Initial	Settling Pond 15 minutes	Settling Pond 30 minutes	Settling Pond 1 hour	Settling Pond 18 hours
Water Chemistry	Total (g/m3)	Al	24	21	x	25	26	29
		Fe	32	33	x	33	33	37
		Mn	0.56	0.72	x	0.62	0.63	0.65
		Ni	0.092	0.111	x	0.103	0.099	0.11
		Zn	0.22	0.23	x	0.24	0.26	0.3
	Dissolved (g/m3)	Al	27	0.139	x	25	29	32
		Fe	33	19.5	x	22	32	28
		Mn	0.53	0.62	x	0.58	0.56	0.62
		Ni	0.087	0.095	x	0.099	0.097	0.11
		Zn	0.21	0.177	x	0.22	0.24	0.26
		Sulphate (g/m3)	590	570	x	580	580	610
Water Quality Parameters		pH	2.55	5.66	x	3.83	3.05	2.74
		DO (%)	30.8	35.8	x	33.1	32.4	53
		EC (µs/cm)	1145	880	x	739	883	1080

Limestone 4 Data Set

Limestone 4 22/12/2017			Inlet AMD	Settling Pond Initial	Settling Pond 15 minutes	Settling Pond 30 minutes	Settling Pond 1 hour	Settling Pond 18 hours
Water Chemistry	Total (g/m3)	Al	49	37	39	46	48	x
		Fe	108*	118*	118*	116*	119*	x
		Mn	0.91	1.02	0.96	0.93	0.92	x
		Ni	0.151	0.158	0.155	0.149	0.152	x
		Zn	0.42	0.4	0.39	0.4	0.4	x
	Dissolved (g/m3)	Al	54	1.81	15.3	39	50	x
		Fe	121*	115*	110*	114*	125*	x
		Mn	0.96	1.06	1.02	0.97	0.94	x
		Ni	0.165	0.158	0.159	0.156	0.158	x
		Zn	0.45	0.4	0.4	0.41	0.42	x
		Sulphate (g/m3)	990	890	900	850	920	x
Water Quality Paramet		pH	2.8	6.2	5.3	3.2	2.9	x
		DO (%)	x	x	x	x	x	x
		EC (µs/cm)	x	x	x	x	x	x

Mussel Shell 1 Data Set

Mussel Shells 1 21/12/2017			Inlet AMD	Settling Pond Initial	Settling Pond 15 minutes	Settling Pond 30 minutes	Settling Pond 1 hour	Settling Pond 18 hours
Water Chemistry	Total (g/m3)	Al	31	25	x	31	32	32
		Fe	32	26	x	30	30	34
		Mn	0.61	0.66	x	0.61	0.62	0.59
		Ni	0.111	0.105	x	0.111	0.108	0.102
		Zn	0.24	0.22	x	0.23	0.24	0.24
	Dissolved (g/m3)	Al	32	21	x	29	32	30
		Fe	31	5.2	x	25	29	33
		Mn	0.6	0.6	x	0.6	0.6	0.56
		Ni	0.105	0.095	x	0.102	0.103	0.1
		Zn	0.26	0.22	x	0.25	0.24	0.24
		Sulphate (g/m3)	600	620	x	620	620	610
Water Quality Parameters		pH	2.5	4.09	x	3.06	2.93	2.68
		DO (%)	37.6	33.8	x	28.6	27.1	52.9
		EC (µs/cm)	1285	843	x	895	935	1109

Mussel Shell 2 Data Set

Mussel Shells 2 22/12/2017			Inlet AMD	Settling Pond Initial	Settling Pond 15 minutes	Settling Pond 30 minutes	Settling Pond 1 hour	Settling Pond 18 hours
Water Chemistry	Total (g/m3)	Al	50	38	42	44	46	49
		Fe	114	106	111	114	116	122
		Mn	0.92	0.86	0.87	0.87	0.86	0.87
		Ni	0.151	0.141	0.143	0.147	0.141	0.148
		Zn	0.44	0.39	0.4	0.39	0.39	0.42
	Dissolved (g/m3)	Al	47	32	40	43	44	55
		Fe	115	90	100	113	119	131
		Mn	0.93	0.9	0.93	0.92	0.89	0.93
		Ni	0.154	0.145	0.151	0.15	0.155	0.154
		Zn	0.42	0.38	0.39	0.4	0.4	0.44
		Sulphate (g/m3)	960	860	830	910	940	1000
Water Quality Parameters		pH	2.8	3.5	3	2.9	2.9	2.9
		DO (%)	x	x	x	x	x	x
		EC (µs/cm)	x	x	x	x	x	x

Mussel Shell 3 Data Set

Mussel Shells 3 23/01/2018			Inlet AMD	Settling Pond Initial	Settling Pond 15 minutes	Settling Pond 30 minutes	Settling Pond 1 hour	Settling Pond 18 hours
Water Chemistry	Total (g/m3)	Al	30	28	30	31	31	30
		Fe	29	49	55	55	58	55
		Mn	0.54	0.75	0.74	0.73	0.74	0.72
		Ni	0.098	0.118	0.119	0.122	0.118	0.122
		Zn	0.29	0.27	0.28	0.28	0.28	0.28
	Dissolved (g/m3)	Al	28	26	33	33	33	34
		Fe	29	28	51	55	55	57
		Mn	0.52	0.7	0.71	0.71	0.7	0.68
		Ni	0.101	0.123	0.121	0.122	0.12	0.128
		Zn	0.28	0.28	0.29	0.29	0.29	0.29
		Sulphate (g/m3)	530	760	730	720	710	700
Water Quality Parameters		pH	2.95	4.04	3.25	3.02	2.97	2.86
		DO (%)	67.8	59.6	48.7	50.1	43.8	56.6
		EC (µs/cm)	2471	1980	2030	2205	2270	2477

Mixed Data Set

Mixed 23/01/2018			Inlet AMD	Settling Pond Initial	Settling Pond 15 minutes	Settling Pond 30 minutes	Settling Pond 1 hour	Settling Pond 18 hours
Water Chemistry	Total (g/m3)	Al	34	24	29	30	31	x
		Fe	61	55	54	56	56	x
		Mn	0.76	0.79	0.74	0.71	0.72	x
		Ni	0.129	0.118	0.116	0.114	0.117	x
		Zn	0.3	0.26	0.27	0.27	0.27	x
	Dissolved (g/m3)	Al	38	13.8	30	33	33	x
		Fe	59	39	46	54	55	x
		Mn	0.75	0.75	0.71	0.71	0.69	x
		Ni	0.124	0.11	0.113	0.112	0.11	x
		Zn	0.3	0.25	0.26	0.27	0.27	x
		Sulphate (g/m3)	760	710	710	700	710	x
Water Quality Parameters		pH	2.75	4.66	3.62	3.24	3.13	x
		DO (%)	29	54.4	47.8	45.7	49.8	x
		EC (µs/cm)	3148	1862	1844	2008	2124	x